

Theoretical Studies of Atomic and Molecular Systems
by Electronic Stress Tensor Theory

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General Introduction

Recently, the importance of nanomaterials is increasing because of technological progress. To predict physical properties of these materials with high accuracy is useful to design nanosize devices. In order to analyze these materials theoretically, to consider quantum effects is important. Because quantum effects are local effects, to use physical quantities based on quantum electrodynamics is useful because it is defined as densities.

In this thesis, according to this background, I perform the analysis using local physical quantities based on rigged quantum electrodynamics (Rigged QED). From this analysis, I obtained basic knowledge of atomic and molecular systems. This thesis is organized by six chapters. Chapter 1 is devoted to reports of atomic systems, and other Chapters are devoted to molecular systems.

In Chapter 1, I analyze the electronic structure of atoms in the first, second and third periods using the electronic kinetic energy density and stress tensor density. These quantities are local quantities based on rigged QED. I compute the zero surfaces of the electronic kinetic energy density, which I call the electronic interfaces (S). Through this analysis, it is shown that, sizes of S exhibit clear periodicity and are comparable to the conventional atomic and ionic radii. I also compute the electronic stress tensor density and its divergence, tension density, of the atoms, and discuss how their electronic structures are characterized by them.

In Chapter 2, I analyze small lithium clusters and hydrocarbon molecules by the electronic stress tensor density. From this analysis, I find three eigenvalues of the electronic stress tensor density of lithium clusters are negative and degenerated. It is just like as the stress tensor of liquid. However, that of hydrocarbon molecules are not degenerated. To quantify the degree of degeneracy, I use the differential eigenvalues of the electronic stress tensor. I show that the differential eigenvalues could be useful indices to evaluate the metallicity or covalency of a chemical bond.

Chapter 3 and 4, some chemical bonds made by atoms usually considered as “metalloids” are analyzed. As an example of “metalloids”, I select molecules which may exist in gas phase of chemical vapor deposition process for GeSbTe alloy. I analyze the electronic structure of them using the electronic stress tensor, with special focus on the chemical bonds between Ge, Sb, and Te atoms. I find that, from the viewpoint of the electronic stress tensor, these bonds have intermediate properties between alkali metals and hydrocarbon molecules. I also study the correlation between the bond order which is defined based on the electronic stress tensor, and energy-related quantities. I find that the correlation between our bond order and the bond dissociation energy is not so strong. However, I have confirmed very strong correlation between our bond order and the force constant. I interpret these results in terms of the energy density on the “Lagrange surface”, which is considered to define the boundary surface of atoms in a molecule in the framework of the electronic stress tensor analysis. In Chapter 5, I analyze the bonding of doped Gallium nanoclusters through the electronic stress tensor density. I find that the degeneracy of chemical bonds of these clusters have also intermediate between alkali metal clusters and hydrocarbon molecules.

In Chapter 6, I perform the calculation of electric conduction. It is confirmed numerically that the tension density is the counter force of the Lorentz force density. This means the tension density cancels out with the acceleration of electron caused by the external field. While I use a simple nonequilibrium Green’s function method, I could confirmed the cancellation with the tension density and Lorentz force density. Because this tension density is free from the relaxation time ansatz and defined as a local quantity, it is useful tool to understand conduction phenomena.

Chapter 1

1 Theoretical Study of Atoms by the Electronic Kinetic Energy Density and Stress Tensor Density

1.1 Introduction

In order to understand the quantum systems from the viewpoint of quantum field theory, in particular quantum electrodynamics (QED), one of the authors has developed the rigged QED (RQED) theory [5, 7, 8, 11, 12] and our group has applied it to various molecular and condensed matter systems [5–7, 7, 8, 8, 9, 9, 10, 10–12, 12, 14–16, 19, 24, 28–30, 32, 33, 33–42]. Due to the field theoretic nature, the theory has local quantities defined at each point in space which are useful to describe quantum systems. Most important quantities are the electronic kinetic energy density and stress tensor density, whose definitions and meanings are presented in the next Section. In this Section, we shall review our past studies using them.

As for the electronic kinetic energy density, our definition is proposed in Ref. [7], which is motivated by the quantum field theoretic consideration, and one of its features is that it is not positive-definite. Then, it has been proposed that the outermost zero surface of the kinetic energy density gives the intrinsic shape of atoms and molecules. This zero surface is designated as “electronic interface” in Ref. [7], and a variety of chemical reactions has been studied using it [6–9, 9, 10, 12, 14–16, 19, 24, 28–30, 34, 41, 42]. We briefly describe some of them below. In Ref. [15], the volume surrounded by the outermost electronic interfaces of a cluster model is defined as its “shape volume” and is used to calculate the electronic dielectric constant of the cluster models of silicate compounds by means of the Clausius-Mossotti equation. In Refs. [34] and [41], local reactivity of Pt clusters and Al clusters regarding hydrogen adsorption has been investigated by mapping the regional chemical potential [7, 32–34], which measures the local chemical reactivity, over the electronic interface of the clusters. The same technique is used to study adsorption of lithium atom on carbon nanotube in Ref. [30].

Meanwhile, using the electronic stress tensor density, together with its divergence, which is called the electronic tension density, new views on chemical bonding has been proposed [5, 7–12]. We have shown that the “Lagrange point”, the point between two atoms where the tension density vanishes, can well characterize the chemical bond between them [32, 33]. We have also shown that the “Lagrange surface”, separatrices of the tension density vector field, may define boundary surfaces of atoms in a molecule [11, 12, 33, 39, 40]. It is pointed out that the eigenvalues and corresponding eigenvectors of the electronic stress tensor in the bonding region play important roles for characterizing types of chemical bonding such as covalency [9, 10] and metallicity [12, 32, 42]. In addition, the bonds between some of semimetal atoms are found to have intermediate nature between covalent and metallic bonds in view of the stress tensor density [33].

Although we have applied the analyses based on the electronic kinetic energy density and stress tensor density to molecular and periodic systems as above, there have not been a systematic application to atoms. It goes without saying that atoms are building blocks for molecules and their electronic kinetic energy density and stress tensor density carry very important information for our analysis. Hence, in this paper, we compute the electronic kinetic energy density, stress tensor density, and tension density of the atoms in the first, second and third periods, and investigate how the atoms are characterized by them.

This paper is organized as follows. In Sec. 2.2, we show our definition of electronic kinetic energy density and stress tensor density. We also describe our computational setups. In Sec. 1.3.1, we investigate the shape of the electronic interfaces of atoms in the first, second and third periods. In Sec. 1.3.2, we study the size of the electronic interfaces and compare with the conventionally defined atomic and ionic radii. In Sec. 1.3.3, we study the integrated electron density inside the electronic

surface. In Sec. 1.3.4, we show the electronic stress tensor density and tension density of the atoms. Finally, Sec. 4.4 is devoted to our conclusion.

1.2 Theory and calculation methods

In this paper, we analyze the electronic structure of atoms using quantities such as the electronic stress tensor density and the kinetic energy density. They are based on the RQED theory [8] and we briefly describe them in this Section. For other studies of quantum systems with the stress tensor in somewhat different contexts and definitions, we refer Refs. [16–31, 51, 52]. We also refer Refs. [53–55] regarding other definitions of kinetic energy density.

The most basic quantity in RQED is the electronic stress tensor density operator $\hat{\tau}_e^{\Pi kl}(x)$ which is defined as [7].

$$\hat{\tau}_e^{\Pi kl}(x) = \frac{i\hbar c}{2} \left[\hat{\psi}(x) \gamma^l \hat{D}_{ek}(x) \hat{\psi}(x) - \left(\hat{D}_{ek}(x) \hat{\psi}(x) \right)^\dagger \gamma^0 \gamma^l \hat{\psi}(x) \right], \quad (1)$$

where $\hat{\psi}(x)$ is the four-component Dirac field operator for electrons with the spacetime coordinate $x = (ct, \vec{r})$. c denotes the speed of light in vacuum, $\hbar$ the reduced Planck constant, and γ^μ ($\mu = 0-3$) the gamma matrices. The dagger as a superscript is used to express Hermite conjugate, and $\hat{\bar{\psi}}(x) \equiv \hat{\psi}^\dagger(x) \gamma^0$. The Latin letter indices like k and l express space coordinates from 1 to 3, and repeated indices implies a summation over 1 to 3. $\hat{D}_{ek}(x)$ is the gauge covariant derivative and it is defined as $\hat{D}_{ek}(x) = \partial_k + i \frac{Z_e e}{\hbar c} \hat{A}_k(x)$, where $Z_e = -1$ and $\hat{A}_k(x)$ is the vector potential of the photon field operator in the Coulomb gauge ($\text{div} \hat{A}(x) = 0$). The important property of this quantity is that the time derivative of the electronic kinetic momentum density operator $\hat{\Pi}_e(x) = \frac{1}{2} \left(i\hbar \hat{\psi}^\dagger(x) \hat{\vec{D}}_e(x) \hat{\psi}(x) - i\hbar \left(\hat{\vec{D}}_e(x) \hat{\psi}(x) \right)^\dagger \cdot \hat{\psi}(x) \right)$ is expressed by the sum of the Lorentz force density operator $\hat{L}_e(x)$ and the tension density operator $\hat{\tau}_e^{\Pi}(x)$, which is the divergence of $\hat{\tau}_e^{\Pi kl}(x)$. Namely,

$$\frac{\partial}{\partial t} \hat{\Pi}_e(x) = \hat{L}_e(x) + \hat{\tau}_e^{\Pi}(x), \quad (2)$$

$$\hat{L}_e(x) = \hat{\vec{E}}(x) \hat{\rho}_e(x) + \frac{1}{c} \hat{\vec{j}}_e(x) \times \hat{\vec{B}}(x), \quad (3)$$

$$\hat{\tau}_e^{\Pi k}(x) = \partial_l \hat{\tau}_e^{\Pi kl}(x) \quad (4)$$

$$\begin{aligned} &= \frac{i\hbar c}{2} \left[\left(\hat{D}_{el}(x) \hat{\psi}(x) \right)^\dagger \gamma^0 \gamma^l \cdot \hat{D}_{ek}(x) \hat{\psi}(x) + \hat{\bar{\psi}}(x) \gamma^l \hat{D}_{ek}(x) \hat{D}_{el}(x) \hat{\psi}(x) \right. \\ &\quad \left. - \left(\hat{D}_{ek}(x) \hat{D}_{el}(x) \hat{\psi}(x) \right)^\dagger \gamma^0 \gamma^l \cdot \hat{\psi}(x) - \left(\hat{D}_{ek}(x) \hat{\psi}(x) \right)^\dagger \gamma^0 \gamma^l \cdot \hat{D}_{el}(x) \hat{\psi}(x) \right] \\ &\quad - \frac{1}{c} \left(\hat{\vec{j}}_e(x) \times \hat{\vec{B}}(x) \right)^k \end{aligned} \quad (5)$$

where $\hat{\rho}_e(x)$ and $\hat{\vec{j}}_e(x)$ are the electronic charge density operator and charge current density operator respectively, and $\hat{\vec{E}}(x)$ and $\hat{\vec{B}}(x)$ denote the electric field operator and magnetic field operator respectively.

As we study nonrelativistic systems in this paper, we approximate the expressions above in the framework of the primary RQED approximation [5, 12]. In this approximation, the small components of the four-component electron field are expressed by the large components as $\hat{\psi}_S(x) \approx -\frac{1}{2mc} i\hbar \sigma^k D_k \hat{\psi}_L(x)$, where m is the electron mass, and the spin-dependent terms are ignored. Then, we take the expectation value of Eq. (34) with respect to the stationary state of the electrostatic Hamiltonian. This leads to

the equilibrium equation as

$$0 = \langle \hat{L}_e^k(x) \rangle + \langle \hat{\tau}_e^{Sk}(x) \rangle = \langle \hat{L}_e^k(x) \rangle + \partial_l \langle \hat{\tau}_e^{Skl}(x) \rangle, \quad (6)$$

which shows the balance between electromagnetic force and quantum field force at each point in space. Since this expresses the fact that the latter force keeps the electrons in the stationary bound state in atomic and molecular systems, we can study them from the viewpoint of quantum field theory by using the stress tensor density and tension density. We express $\langle \hat{\tau}_e^{Sk}(x) \rangle$ and $\langle \hat{\tau}_e^{Skl}(x) \rangle$ respectively $\tau_e^{Sk}(\vec{r})$ and $\tau_e^{Skl}(\vec{r})$ for simplicity. Note that, as we consider stationary state, we write only spatial coordinate $\vec{r}$. Writing explicitly,

$$\begin{aligned} \tau_e^{Skl}(\vec{r}) = & \frac{\hbar^2}{4m} \sum_i \nu_i \left[\psi_i^*(\vec{r}) \frac{\partial^2 \psi_i(\vec{r})}{\partial x^k \partial x^l} - \frac{\partial \psi_i^*(\vec{r})}{\partial x^k} \frac{\partial \psi_i(\vec{r})}{\partial x^l} \right. \\ & \left. + \frac{\partial^2 \psi_i^*(\vec{r})}{\partial x^k \partial x^l} \psi_i(\vec{r}) - \frac{\partial \psi_i^*(\vec{r})}{\partial x^l} \frac{\partial \psi_i(\vec{r})}{\partial x^k} \right], \end{aligned} \quad (7)$$

$$\begin{aligned} \tau_e^{Sk}(\vec{r}) = & \partial_l \tau_e^{Skl}(\vec{r}) \\ = & \frac{\hbar^2}{4m} \sum_i \nu_i \left[\psi_i^*(\vec{r}) \frac{\partial \Delta \psi_i(\vec{r})}{\partial x^k} - \frac{\partial \psi_i^*(\vec{r})}{\partial x^k} \Delta \psi_i(\vec{r}) \right. \\ & \left. + \frac{\partial \Delta \psi_i^*(\vec{r})}{\partial x^k} \psi_i(\vec{r}) - \Delta \psi_i^*(\vec{r}) \frac{\partial \psi_i(\vec{r})}{\partial x^k} \right], \end{aligned} \quad (8)$$

where $\psi_i(\vec{r})$ is the i th natural orbital and ν_i is its occupation number. Δ denotes the Laplacian, $\Delta \equiv \sum_{k=1}^3 (\partial/\partial x^k)^2$. The eigenvalue of the symmetric tensor $\overset{\leftrightarrow}{\tau}_e^S$ is the principal stress and the eigenvector is the principal axis. We denote the eigenvalues as $\tau_e^{S11}(\vec{r}) \leq \tau_e^{S22}(\vec{r}) \leq \tau_e^{S33}(\vec{r})$.

We note that the tension density in the form of Eq. (40) is same as what is called quantum force density in Refs. [25, 56]. Then, the Ehrenfest force field used in Refs. [25, 56–58] (and the force density in Ref. [17], Eq. (24)) is same as the tension density with the minus sign in the stationary state. Another note is on the ambiguity of the stress tensor density. It is not defined uniquely since mathematically any tensor whose divergence is zero can be added to. Our stress tensor density Eq. (39) is same as the one in Ref. [17], Eq. (22). The difference in the definitions and approximations are discussed recently in Refs. [29–31, 51, 52]. We advocate the use of Eq. (39) since it comes from the stress tensor density operator Eq. (32), which is a minimal combination respecting the Lorentz covariance, gauge invariance and hermiticity. Moreover, this definition turns out to be phenomenologically useful as shown by our works mentioned in the previous Section.

Another important quantity in the RQED is the electronic kinetic energy density operator defined as [7],

$$\hat{T}_e(x) = -\frac{\hbar^2}{2m} \cdot \frac{1}{2} \left(\hat{\psi}^\dagger(x) \hat{D}_e^2(x) \hat{\psi}(x) + \left(\hat{D}_e^2(x) \hat{\psi}(x) \right)^\dagger \cdot \hat{\psi}(x) \right). \quad (9)$$

As is done for the electronic stress tensor density operator, we apply the primary RQED approximation to Eq. (43) and take the expectation value with respect to the stationary state of the electrostatic Hamiltonian. Then, we obtain the definition for the electronic kinetic energy density as

$$n_{T_e}(\vec{r}) = -\frac{\hbar^2}{4m} \sum_i \nu_i [\psi_i^*(\vec{r}) \Delta \psi_i(\vec{r}) + \Delta \psi_i^*(\vec{r}) \cdot \psi_i(\vec{r})]. \quad (10)$$

Note that our definition of the electronic kinetic energy density is not positive-definite. Using $n_{T_e}(\vec{r})$, we can divide the whole space into three types of region as follows [7]:

$$R_D = \{ \vec{r} | n_{T_e}(\vec{r}) > 0 \} \quad : \text{electronic drop region} \quad (11)$$

$$S = \{ \vec{r} | n_{T_e}(\vec{r}) = 0 \} \quad : \text{electronic interface} \quad (12)$$

$$R_A = \{ \vec{r} | n_{T_e}(\vec{r}) < 0 \} \quad : \text{electronic atmosphere region} \quad (13)$$

In R_D , the electronic drop region, the classically allowed motion of electron is guaranteed and the electron density is amply accumulated. In R_A , the electronic atmosphere region, the motion of electron is classically forbidden and the electron density is dried up. The boundary S between R_D and R_A is called the electronic interface and corresponds to a turning point. The outermost S can give a clear image of the intrinsic shape of atoms and molecules and is, therefore, an important region in particular.

Thus, in our method, the outermost electronic interface defines the shape of atoms and molecules. We note that it is frequently defined by the isosurface of the electron density. The values of isosurface like 0.001 a.u. and 0.002 a.u. are proposed in Refs. [59–61], and there is some arbitrariness. In contrast, since our definition uses the zero isosurface of non-positive-definite quantity $n_{T_e}(\vec{r})$, there is no such arbitrariness. It is true that there is ambiguity regarding the definition of the kinetic energy density [53–55], which is sometimes defined as a positive definite quantity. Our definition comes from the electronic kinetic energy density operator, Eq. (43), whose definition is in turn motivated by the relativistic energy dispersion relation between the energy E and momentum p : $E = \sqrt{(pc)^2 + (mc^2)^2} \approx mc^2 + \frac{p^2}{2m}$. We take the kinetic energy part $\frac{p^2}{2m}$, replace p_k by $i\hbar\hat{D}_{ek}$ as a usual quantization rule under the existence of the electromagnetic field, and construct a field operator by sandwiching between $\hat{\psi}^\dagger(x)$ and $\hat{\psi}(x)$. We then make the field operator Hermitian as Eq. (43) by adding the Hermitian conjugate and divide by two. We advocate the use of definition (44) since it comes from such a field theoretic construction.

In the end of this Section, we summarize our computational setups. The electronic structures used in this paper are obtained by the Gaussian 09 [58]. The computation is performed by the unrestricted Hartree-Fock (UHF) method using the cc-pV5Z basis set [63]. To compute the aforementioned quantities such as Eqs. (39), (40) and (44) from the electronic structure data, we use the QEDynamics package [34] developed in our group.

1.3 Results and discussion

1.3.1 Shape of the electronic interface of atoms

In Fig. 1, we show the electronic interface, S , for atoms of elements in the first, second and third periods. Spin multiplicities are chosen to give their ground states, whose term symbols are shown in Table 1 [65]. In the case of open-shell systems, the expectation values of S^2 are reported in Table 1, showing that spin contaminations are small. As for the electron configuration regarding the p orbitals, we choose them to be occupied in the alphabetical order p_x, p_y, p_z . For instance, the configuration of B is $1s^2 2s^2 2p_x^1$, C is $1s^2 2s^2 2p_x^1 2p_y^1$ and so on. In each panel, the atomic nucleus is placed at the origin. For all of these elements, the S 's have axial symmetry, and some of them have spherical symmetry. We omit the information of the value of the kinetic energy density in the figure, but we can recognize its sign by noting that the region in the neighborhood of the nucleus should have positive kinetic energy density, that is to say R_D . Going outward, R_A and R_D appear alternately bounded by S and we should have R_A at infinity. In Fig. 2, we show the cross Sections of S 's to inspect their detailed structures. Again, in each panel, the atomic nucleus is placed at the origin. Since we plot to make the symmetry axis coincides with the horizontal axis, the axes may differ from panel to panel. For example, in the panel of B, the horizontal axis corresponds to x -axis, but it corresponds to z -axis in the panel of C.

We can see that the shapes found in Figs. 1 and 2 have the symmetry which is expected from the electron configurations of each atom. Namely, while the S 's of H, He, Li, Be, N, Ne, Na, Mg, P and

Ar are spherically symmetric, those of the other elements, B, C, O, F, Al, Si, S and Cl are only axially symmetric. In detail, B, O, Al and S are axially symmetric with respect to the x -axis, reflecting the configuration of the outermost p subshell: np_x^1 for B and Al, and $np_x^2 np_y^1 np_z^1$ for O and S. As for C, F, Si and Cl, they are axially symmetric with respect to the z -axis due to the configuration $np_x^1 np_y^1$ for C and Si, and $np_x^2 np_y^2 np_z^1$ for F and Cl. Also, the periodicity regarding the size of S is manifestly shown: the size increases as the period increase in the same row, and decreases as the atomic number increases in the same period.

The common feature for all the elements is that they clearly have outermost S which is homeomorphic to 2-sphere (two-dimensional surface of a ball). We denote the outermost S as S_{outer} . We next notice that, while H, He and Ne have only one S (only S_{outer}), the others have multiple S 's. As for those with multiple S 's, most of them have two S 's inside S_{outer} , and in addition, they are both homeomorphic to 2-sphere and the larger S encloses the smaller ones. When such a structure is found, we denote the innermost S as S_{inner} . In every case, since these two S 's are very close to each other, it seems that a relatively thin spherical shell region of R_A is formed inside S_{outer} . In other words, the region inside S_{outer} appears to be divided into two R_D 's by the nearly spherical-shell-shaped R_A . Exceptions are O and F. As for O, it has a single S which is homeomorphic to 2-torus (a solid-torus-shaped R_A) inside S_{outer} . As for F, it has two S 's inside S_{outer} but they do not form a shell-like region and just two disconnected R_A 's are formed. (Actually, these features are so fine that it is very hard to see in Fig 1. They can be more easily imagined from Fig. 2 by rotating the cross Section with respect to horizontal axis.) Thus, for both cases, there is only one connected region of R_D , and S_{inner} is not formed. We check whether these features for O and F may change if we use wavefunctions computed by the restricted open-shell HF (ROHF) method. We find that the ROHF gives visually undistinguishable S 's for O and F. We discuss why they form such R_A 's below.

On looking at these structures, one might associate the pattern of S as the electron shell structure in atoms. It is tempting to associate R_D which is divided by thin R_A as the shell structure. The single R_D seen in H and He can be associated with K shell. From Li to N, they have two R_D 's which can be associated with K and L shells. However, this breaks down at O, F and Ne, which have only one R_D as pointed out above. Moreover, from Na to Ar, which should have K, L and M shells, they only have two R_D 's. Therefore, S is not a good indicator of the atomic shell structure. Instead, it may be better to consider two R_D 's separated by the thin R_A region as the manifestation of “core” and “valence” regions in some sense. In particular, the core shell can be defined as R_D enclosed by S_{inner} if it exists. The irregularities concerning O, F and Ne are interpreted as follows. As for O, if there were only three electrons in the $2p$ subshell as $2p_x^1 2p_y^1 2p_z^1$, the R_A would be shell-shaped region like the one in N. Since there exists one more $2p_x$ electron, the probability of the electron in the core region is higher so that shell-shaped R_A is deformed to be solid-torus shape as if penetrated by the $2p_x$ orbital. Note that the torus's hole is opened in the direction of x -axis, which is consistent with the direction of $2p_x$ orbital. As for F, one more electron in the $2p_y$ orbital is added and it again penetrates in the core region. Then, the torus-shaped R_A is split in the y -direction, and two R_A 's remain on the z -axis. Finally, in Ne, the addition of one more electron in the $2p_z$ orbital completely erases these remaining R_A 's.

1.3.2 Size of the electronic interface and comparison with atomic and ionic radii

In this Section, we quantify the size of S_{outer} and S_{inner} in the following manner. When S is spherical, the size can be readily defined by its radius. However, as we have seen in Sec. 1.3.1, some of the elements have non-spherical S . In that case, we report the longest and shortest distances between nucleus and S , respectively as the upper and lower limits. Also, as the central value, we report an averaged distance between nucleus and S by computing the radius of the ball whose volume is equal to the S 's volume. As for O and F, for which S_{inner} is not defined, we just report the shortest distance between nucleus and R_A inside S_{outer} . The results are summarized in Table 1 and Fig. 3. We can confirm the periodicity regarding the size of S_{outer} and S_{inner} in the figure. We note that, for S_{inner} , the deviation from sphere

is so small that we cannot recognize the error bars. As for O and F, the same quantities are computed using the ROHF wavefunctions. We find that S_{outer} and S_{inner} of O are respectively $0.9610^{+0.0446}_{-0.0313}$ and $[0.1533]$, and those of F are respectively $0.8623^{+0.0159}_{-0.0451}$ and $[0.1378]$, which are almost identical to the UHF results in Table 1.

At this stage, it is instructive to examine S of the cations which are constructed by removing all the electrons in the outermost shell, for example, B^{3+} , C^{4+} , N^{5+} and so on. Since the cations exhibit multiple S 's, which are considered to be numerical artefacts, we adopt innermost S as S_{outer} for the cations (see Fig S1). As a result, we find that all these cations have only one S (only S_{outer}) which is spherical, as expected. The S_{outer} 's radii of the cations are summarized in Table 1 and Fig. 3. Then, we see that S_{inner} of each atom is almost same as the S_{outer} of the corresponding cation. This is another reason that we wish to interpret R_D bounded by S_{inner} as a core region. (In addition, we have observed in our past works that such core regions defined by S are preserved in molecules. For example, Figs. 2, 3, 7 and 8 of Ref. [42] for Li and Fig. 2 of Ref. [33] for C.) As for O and F, although they do not have S_{inner} , the sizes of R_A regions inside their S_{outer} are very close to S_{outer} of O^{+6} and F^{+7} . This supports our interpretation for the irregular shapes of R_A regions in O and F, that they are caused by the penetration of electrons in $2p$ orbitals into their core regions, as argued in the end of Sec. 1.3.1.

Next, in Fig. 3, we plot atomic radii from Ref. [8] and ionic radii from Ref. [9], along with the size of S_{outer} and S_{inner} as determined above. We quote two types of ionic radii, crystal radii and univalent radii, which appear in Ref. [9]. The crystal radii of multivalent ions are defined so that the sum of two radii is equal to the actual equilibrium interionic distance in a crystal. For example, the univalent radius is applied to $Mg^{2+}F_2^-$ while the crystal radius to $Mg^{2+}O^{2-}$. We find that the atomic radii are comparable to the size of S_{outer} , in a sense that they have similar periodicity and differ by a factor of two at most. Similarly, we can say that the ionic radii are comparable to the size of S_{inner} . However, taking a closer look, the atomic radii are always smaller than the size of S_{outer} . The univalent ionic radii are always larger than the size of S_{inner} . Although some of the crystal ionic radii are very close to the size of S_{inner} , since the slopes with respect to the nuclear charge are different, the agreement should be considered as a mere coincidence.

Such a disagreement between the atomic radii and S_{outer} 's size, and the one between the ionic radii and S_{inner} 's size, are not surprising. This is because, while the atomic/ionic radii are defined to give equilibrium internuclear distance in compounds and crystals on summing two radii, the sizes of S_{outer} and S_{inner} are defined for isolated atoms. As for the atomic radii, we can consider that the formation of covalent bond just begins when the S_{outer} 's of two atoms touch each other (this moment is called the "electronic transition state" [7]). Then, after the bond formation, at the equilibrium, the interatomic distance is shorter than the sum of the radii of S_{outer} of the two atoms. Therefore, the formation of chemical bonding makes the atomic radii smaller than the S_{outer} 's sizes. As for the ionic radii, let us consider $X^{n+}Y_n^-$ for the univalent radii and $X^{n+}Y^{n-}$ for the crystal radii of multivalent ions. The simplified description of ionic bonding is that, first, the valence electrons of X move from X to Y, and then, they are bonded by the electrostatic force between X cation and Y anion. Then, the ionic radii of X^{n+} should be about the size of S_{inner} of X. However, as is well known, this picture is oversimplified and some fraction of the valence electrons remain at X. This is the reason why the univalent radii are larger than the S_{inner} 's sizes. Similar consideration applies for the crystal radii of multivalent ions, but in this case, the electrostatic attraction is so strong that the interionic distance becomes much shorter. This is the reason why the crystal radii are smaller than the S_{inner} 's sizes for large n .

1.3.3 Integrated electron density inside the electronic interface

In this Section, we study S from the viewpoint of amount of electrons enclosed within it. As is mentioned in Sec. 2.2, R_D is the region where classically allowed motion of electron is guaranteed and the electron density is amply accumulated. We demonstrate this point by integrating electron density over R_D in each atom. In other words, we integrate over the region inside S_{outer} omitting R_A , if it exists inside

S_{outer} like the cases of O and F. The results are shown in Fig. 4, where the upper panel shows the integrated electron density and the lower panel shows its ratio to the total electron number. We can confirm that electrons have high probability, about 70%–90%, to be found in R_D . The results for the cations are also shown and we find that the ratios fall within the similar range.

We note here on the analytic result for the ground state of the hydrogen-like atom with nuclear charge Z . When we use the analytic wave function, R_D is found to be a ball whose radius is $2/Z$ bohr [7], and the integration of electronic density over there is $1 - 13/e^4 \approx 0.761897$, where e is the Euler’s number. This integration does not depend of Z . Our numerical integration for H reproduces this value with the error less than 1%.

In Fig. 4, upper panel, and in Table 2, we also show the results of integration only over the core region defined as the region enclosed by S_{inner} . For the atoms which do not exhibit S_{inner} (H, He, O, F and Ne), data points are omitted. The results are almost same as those over the region within S_{outer} of corresponding cations, which are expected from the closeness of their sizes as seen in the previous Section. The integrated electron density of core region turns out to be about 1.5–1.7 for the atoms of the second period and about 8.9–9.4 for those of the third period. In Table 2, we also quote core radius and core electron number derived from some of the shell structure descriptors in the literature, Ref. [68] considering “ideal shells”, Ref. [69] using the electron localization function, and Ref. [70] based on inhomogeneity measures of the electron density in connection with the electron localizability indicator. Our values based on S_{inner} are generally much smaller than the others, indicating that the core region defined by S_{inner} has somewhat different meaning from the one based on the shell structure descriptors. Although our core electron numbers are away from the values of the ideal shells [68], the relation between core-valence partitioning in the orbital picture and one in real space is not straightforward and whether a partitioning scheme has to be an ideal one is not evident [71]. We believe that our definition of a core region using the electronic interface is worth investigating further, along with other definitions in the literature [69, 70, 72–85], for describing chemical bonding and reactions.

1.3.4 Stress tensor density and tension density

In this Section, we examine the electronic stress tensor density and tension density of the atoms. We start from the tension density, which is shown in Fig. 5 as black arrows. They are normalized and their norm is expressed by the color map. The electronic interfaces are plotted by the black solid lines, which are same as Fig. 2. We see that, for all the atoms we examine, the arrows go radially from the center, at which the nucleus is located. There are some exceptions but they are found at very far outside S_{outer} so that we may regard them as numerical artifacts. Such artifacts have been discussed in Ref. [37] by comparing the tension density computed from the exact solution for H_2^+ with one from solutions using gaussian basis sets. Recently, Ref. [58] has examined the artifacts of the Ehrenfest force density (which is the minus of the tension density) based on the Slater-type orbitals. This pattern of the atomic tension density that the vector field points from the nucleus to outside of the atom is important for the formation of “Lagrange surface” of a molecule [11, 12, 33, 39, 40]. The Lagrange surface of a molecule AB composed of atoms A and B is defined as follows [11, 12]. The Heisenberg uncertainty principle allows electron to diffuse away from each atomic center it belongs, and the diffusion force is the tension compensating the Lorentz force exerting from each atomic center as expressed by Eq. (38). The tension vector fields originated from A and B mutually collide to form a separatrix that discriminates each region of atomic center. The separatrix is called the Lagrange surface. We refer Fig. 2 of Ref. [11] or Fig. 12.3 of Ref. [12] for the schematic picture of the Lagrange surface, and Fig. 7 of Ref. [33] for a computed example. This picture of local equilibrium in the stationary state of a molecule assumes that the tension of an isolated atom has a pattern such that the vectors radiate from the nucleus. Although there is no mathematical proof that all the atoms exhibits the pattern, our calculation shows that the pattern holds for those in the first, second and third periods.

Here, some comments on the Lagrange surface may be in order. In our method, the boundary

between atoms are defined by this Lagrange surface (the outer boundary is defined by the outermost electronic interface as described in Sec. 2.2). Although this is conceptually similar to the so-called interatomic surface [60,61], the definitions are different. The interatomic surface is defined as a separatrix of the gradient vector field of the electron density whereas the Lagrange surface is one of the tension vector field. As is noted in Sec. 2.2, the tension density and the Ehrenfest force density is only different by a minus sign so that separatrices in these vector fields coincide. Therefore, the recent work in Ref. [56] on the partitioning scheme based on separatrices of the Ehrenfest force field is same as one using the tension density and Lagrange surface in our terminology.

Next, we move on to study the stress tensor density. In Fig. 6, the largest eigenvalue of the stress tensor $\tau_e^{S33}(\vec{r})$ is plotted as a color map and corresponding eigenvector is expressed by a black rod. One may notice that there are some regions in B, Al and S where no rod is shown. There, the eigenvectors are directed perpendicular to the plane so that a rod becomes a dot and not shown. Also, one may notice that some rods are made thicker and colored orange, for example in Li and Be. At these points, the largest two eigenvalues, $\tau_e^{S33}(\vec{r})$ and $\tau_e^{S22}(\vec{r})$, are degenerate. For the atoms we have computed here, one of the two eigenvectors corresponding to the degenerated eigenvalue is always in the direction perpendicular to the plane so that only one (thick orange) rod appears at each point. In Fig. 6, the zero isosurfaces of the eigenvalue are plotted by the red solid lines and the electronic interfaces are plotted by the black solid lines. As for the zero isosurfaces of the eigenvalue, we note that some of them appear as numerical artifacts. This is most conspicuously shown in H. Although the analytic wave function of the H atom gives $\tau_e^{S33}(\vec{r}) = 0$ everywhere [9], we see several zero-surfaces in the figure of H. They are numerical artifacts caused by the oscillatory behavior around zero, which is in turn due to the approximate wave function constructed from gaussian functions. Then, it is not hard to imagine similar artificial zero-surfaces may appear when $\tau_e^{S33}(\vec{r})$ is close to zero, typically far away from the nucleus. Although we cannot tell which zero-surface is the artifact a priori, we may regard the one which locates well outside S_{outer} as artificial.

Before analyzing the stress tensor of the atoms further, it may be instructive here to summarize our past findings on the stress tensor of molecules some more in detail than Sec. 4.1. In Ref. [9], it has been proposed that the bonding region with covalency can be characterized and visualized by the “spindle structure”, where the largest eigenvalue of the electronic stress tensor is positive (tensile stress) and the corresponding eigenvectors form a bundle of flow lines that connects nuclei. In other words, the positive largest eigenvalue can be associated with the Lewis electron pair formation. In contrast, the eigenvalue can be negative (compressive stress) at bonding region for several cases. For one thing, it is found at a very short bond such as C_2H_2 [10, 33, 39]. It is explained that the internuclear region of C_2H_2 , which should be covalent, is overwhelmed by the atomic compressive stress around the C nuclei as they are so close. The atomic compressive stress in turn is attributed to marginal stability around atoms [10]. Another case is when a bond exhibits metallicity [12, 32, 33, 42]. In this case, the eigenvalues are not only negative but also degenerate, $0 > \tau_e^{S33}(\vec{r}) \approx \tau_e^{S22}(\vec{r}) \approx \tau_e^{S11}(\vec{r})$, reflecting the liquid-like (compressive and isotropic) nature of metallicity of chemical bonding. (In passing, for the case of C_2H_2 , the eigenvalues are not degenerate, $0 > \tau_e^{S33}(\vec{r}) > \tau_e^{S22}(\vec{r}) \approx \tau_e^{S11}(\vec{r})$ [32, 42].)

With these in mind, we will now take a look at Fig. 6. An overall rough trend is that the eigenvalue is negative, manifesting the atomic compressive stress [10]. There are, however, some places with positive eigenvalues (we omit the discussion for H, whose largest eigenvalue is zero everywhere as mentioned above, as it has already been discussed in our previous works [7, 9, 10]). We see the positive eigenvalue regions in: (i) entire R_D of He, (ii) central regions of the atoms in the second period, and (iii) outer regions of R_D including some parts or all of S_{outer} in O, F, and Ne. The case (i) is interpreted as due to the electron pairing of $1s^2$. The case (ii) is considered to have the same origin as the case (i), though the positive regions shrink as outer shells pile up. As we go to the third period, such positive regions disappear from the core regions. It seems that the tensile stress caused by the electron pairing is immersed under the atomic compressive stress. The case (iii) is considered to occur due to the electron pairing in the $2p$ shell. As for O, the electron pairing of $2p_x^2$ is manifested as the positive eigenvalue

regions, so that they locate in the x -directions. Similarly, the electron pairing of $2p_x^2$ and $2p_y^2$ in F leads to the positive eigenvalue region axially symmetric with respect to the z -axis, and that of $2p_x^2$, $2p_y^2$, and $2p_z^2$ in Ne results in the spherically symmetric positive eigenvalue region. Again, it seems that such tensile stress is immersed under the atomic compressive one in the third period atoms.

Another noticeable feature, such as found in Li, is that the valence region has two layers. The outside layer consists of the eigenvectors going radially, and the inside layer is characterized by the two degenerate eigenvalues whose eigenvectors are perpendicular to the radial direction. The degenerate character of the inside layer has been found to appear in a Li_2 molecule or other small Li clusters [42]. We have pointed out in Ref. [42] that, in view of the stress tensor density, chemical bonding of the Li clusters, even Li_2 , is characterized by a lack of directionality which is represented by the degenerate eigenvalues and corresponding eigenvectors. The stress tensor density of the Li atom is found to already exhibit such a degenerate feature. We see in Fig. 6 that Be, Na, Mg, P, and Ar exhibit similar pattern to Li. How these degenerate features may play a role in compounds and clusters involving these atoms is interesting question to ask, and this is work in progress in our group.

1.4 Conclusion

In this paper, we have analyzed the electronic structure of atoms in the first, second and third periods using the electronic kinetic energy density, tension density, and stress tensor density, which are local quantities motivated by quantum field theoretic consideration, specifically RQED.

We have used the concept of the electronic interface S , which has been defined in Ref. [7] as the zero surface of non-positive-definite kinetic energy density to illustrate the shape of atoms and molecules. We have investigated the shape of S and found that S_{outer} , the outermost S , exhibits the symmetry which is expected from the electron configurations of each atom. We have pointed out that, in most cases, the region inside S_{outer} is divided into two R_D 's by the nearly spherical-shell-shaped R_A . For these two R_D 's, we have associated the inner R_D as the core region and the outer R_D as the valence region. This interpretation is supported by the size of S_{outer} of the cations which are constructed by removing all the electrons in the outermost shell. We have denoted the boundary surface of core shell as S_{inner} , and have investigated the size of S_{outer} and S_{inner} . Then, we have found the clear periodicity for the size of S_{outer} and S_{inner} with respect to the nuclear charge. The size of S_{outer} and S_{inner} have been compared respectively with the atomic and ionic radii in the literature, and their difference has been discussed.

As for the tension density, all of the atoms we have examined exhibit a common pattern that the vector field points from the nucleus to outside of the atom. Such radial pattern of the atomic tension density is important to be confirmed, as it is necessary for the universal local equilibrium picture of electronic stationary state of a molecule with the Lagrange surface [11,12]. As for the stress tensor density, we have studied its largest eigenvalue and corresponding eigenvector, which has played an important role in our chemical bonding and reactivity analyses on molecular systems. We have first confirmed that the atoms generally exhibit negative eigenvalues, the compressive stress, by which marginal stability around atoms is represented [10]. We have also found some regions with positive eigenvalue, the tensile stress, for some atoms. They can be interpreted as the tensile stress associated with the covalency which describes the electron pairing [9,10].

We believe that this work has revealed novel aspects of electronic structure of atoms in view of the electronic kinetic energy density and stress tensor density. At the same time, it raises many interesting issues that will need further research. First of all, note that our interpretation here is based on the real-valued wave functions obtained by the HF method. Configuration interaction method should be used to respect appropriate symmetry of wave functions, which will be used to study the electronic interfaces and stress tensor in our future work. It is also necessary to study the atoms in higher periods to confirm the interpretation presented in this study and to investigate such effects as the lanthanide contraction and contraction of the heavy elements by relativistic effects. In addition to the electronic

kinetic energy density and stress tensor density, one of the authors has proposed novel quantities related to the electronic spin: spin torque density, zeta force density and spin vorticity [5, 11, 12, 22, 86, 88, 89]. The study through these quantities would give us further new insight into our understanding of electronic structure of atoms, and chemistry.

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	Neutral atom					Cation		Radius	
	State	$\langle S^2 \rangle$	Ratio	S_{outer}	S_{inner}	Ratio	S_{outer}	Covalent	Ionic
H	$^2S_{1/2}$	0.750	0.767	1.067	—	—	—	0.32	—
He	1S_0	—	0.731	0.623	—	—	—	0.46	—
Li	$^2S_{1/2}$	0.750	0.740	2.6953	0.3915	0.741	0.3910	1.33	0.60(0.60)
Be	1S_0	—	0.744	1.7901	0.2866	0.748	0.2858	1.02	0.31(0.44)
B	$^2P_{1/2}$	0.761	0.782	$1.4855^{+0.2250}_{-0.1630}$	$0.2304^{+0.0066}_{-0.0039}$	0.753	0.2259	0.85	0.20(0.35)
C	3P_0	2.010	0.811	$1.2530^{+0.0640}_{-0.1820}$	$0.1955^{+0.0041}_{-0.0086}$	0.755	0.1862	0.75	0.15(0.29)
N	$^4S_{3/2}$	3.758	0.839	1.0828	0.1730	0.756	0.1584	0.71	0.11(0.25)
O	3P_2	2.009	0.871	$0.9602^{+0.0539}_{-0.0333}$	[0.1535]	0.756	0.1377	0.63	0.09(0.22)
F	$^2P_{3/2}$	0.754	0.887	$0.8623^{+0.0173}_{-0.0445}$	[0.1379]	0.757	0.1219	0.64	0.07(0.19)
Ne	1S_0	—	0.889	0.7804	—	0.758	0.1093	0.67	—
Na	$^2S_{1/2}$	0.750	0.870	2.9140	0.6521	0.893	0.6515	1.55	0.95(0.95)
Mg	1S_0	—	0.857	2.1848	0.5587	0.893	0.5569	1.39	0.65(0.82)
Al	$^2P_{1/2}$	0.771	0.868	$2.0520^{+0.4548}_{-0.3297}$	$0.4959^{+0.0000}_{-0.0015}$	0.896	0.4922	1.26	0.50(0.72)
Si	3P_0	2.016	0.875	$1.8148^{+0.1142}_{-0.3351}$	$0.4446^{+0.0002}_{-0.0008}$	0.897	0.4396	1.16	0.41(0.65)
P	$^4S_{3/2}$	3.751	0.879	1.6028	0.4032	0.898	0.3972	1.11	0.34(0.59)
S	3P_2	2.013	0.884	$1.4444^{+0.0458}_{-0.0222}$	$0.3706^{+0.0005}_{-0.0009}$	0.898	0.3620	1.03	0.29(0.53)
Cl	$^2P_{3/2}$	0.761	0.890	$1.3107^{+0.0115}_{-0.0214}$	$0.3440^{+0.0003}_{-0.0020}$	0.898	0.3329	0.99	0.26(0.49)
Ar	1S_0	—	0.898	1.1955	0.3221	0.899	0.3082	0.96	—

Table 1: The ratio refers to the quotient of electron density integrated over R_D inside S_{outer} divided by the total electron number. Numbers in the columns of S_{outer} and S_{inner} are the measures of their size which are described in Sec. 1.3.2, in units of Å. Covalent radii are taken from Ref. [8] and ionic radii from Ref. [9], also in units of Å. Two types of ionic radii, the crystal radii and univalent radii, are quoted, and the latter is denoted in the parentheses.

	Core radius				Core electron number			
	S_{inner}	[68]	[69]	[70]	S_{inner}	[68]	[69]	[70]
Li	0.3915	0.81073	0.810	0.6949	1.48	2	2.0	1.9
Be	0.2866	0.52136	0.540	0.4316	1.53	2	2.0	1.9
B	0.2304	0.37144	0.40	0.3082	1.57	2	2.0	1.9
C	0.1955	0.28424	0.31	0.2347	1.62	2	2.1	1.8
N	0.1730	0.22855	0.25	0.1869	1.69	2	2.1	1.8
O	[0.1535]	0.19065	0.21	0.1542	—	2	2.1	1.7
F	[0.1379]	0.16285	0.18	0.1301	—	2	2.1	1.7
Ne	—	0.14172	0.16	0.1116	—	2	2.1	1.7
Na	0.6521	1.12544	1.130	1.0123	8.92	10	10.1	9.9
Mg	0.5587	0.86178	0.892	0.7484	8.96	10	10.1	9.8
Al	0.4959	0.71646	0.738	0.6152	9.03	10	10.1	9.7
Si	0.4446	0.61204	0.626	0.5209	9.08	10	10.1	9.7
P	0.4032	0.53293	0.542	0.4509	9.14	10	10.1	9.5
S	0.3706	0.47150	0.483	0.3974	9.22	10	10.1	9.5
Cl	0.3440	0.42206	0.432	0.3546	9.29	10	10.1	9.4
Ar	0.3221	0.38145	0.391	0.3199	9.39	10	10.1	9.4

Table 2: Core radius and core electron number derived from S_{inner} and those from the shell structure descriptors proposed in Refs. [68–70] (the core electron numbers of Ref. [68] are 2 for the atoms of the second period and 10 for those of the third period by definition). The core radius is in units of Å. The core radius defined by S_{inner} is quoted from Table 1.

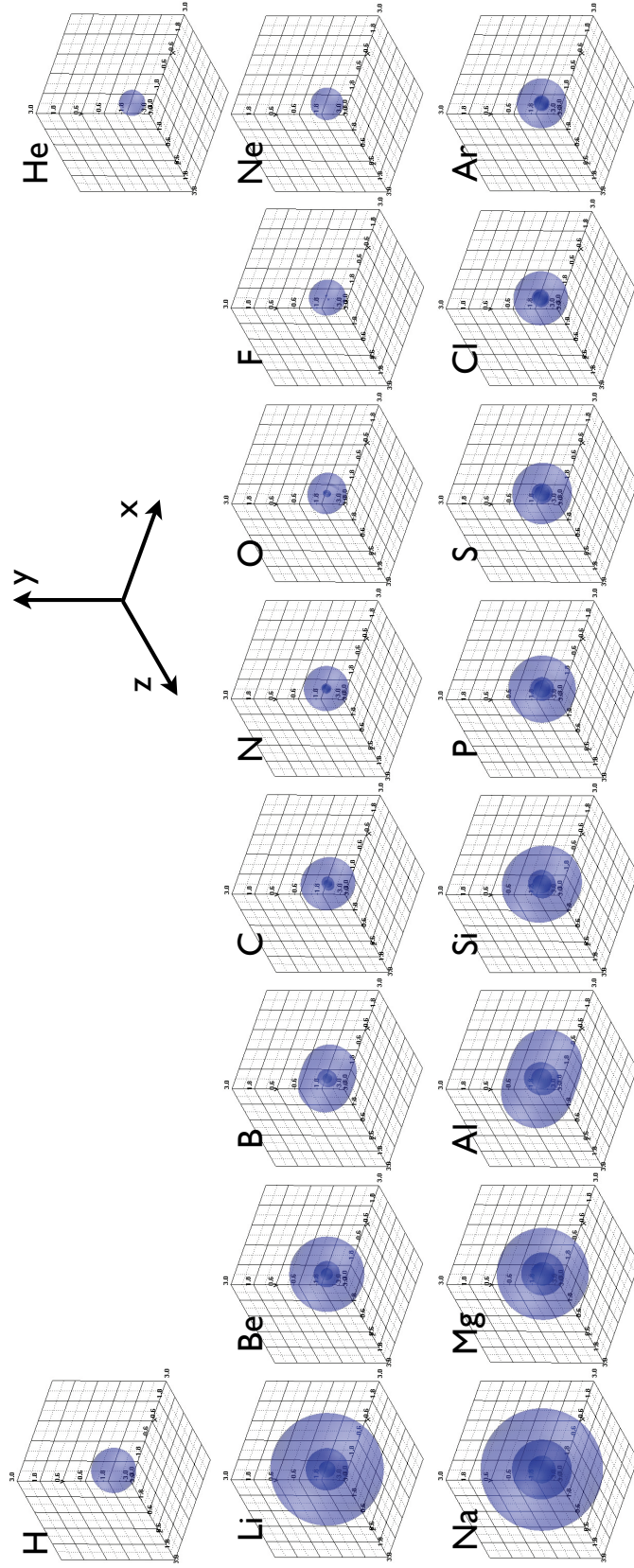


Fig. 1: Electronic interfaces of the atoms. The units are in $\text{\AA}$.

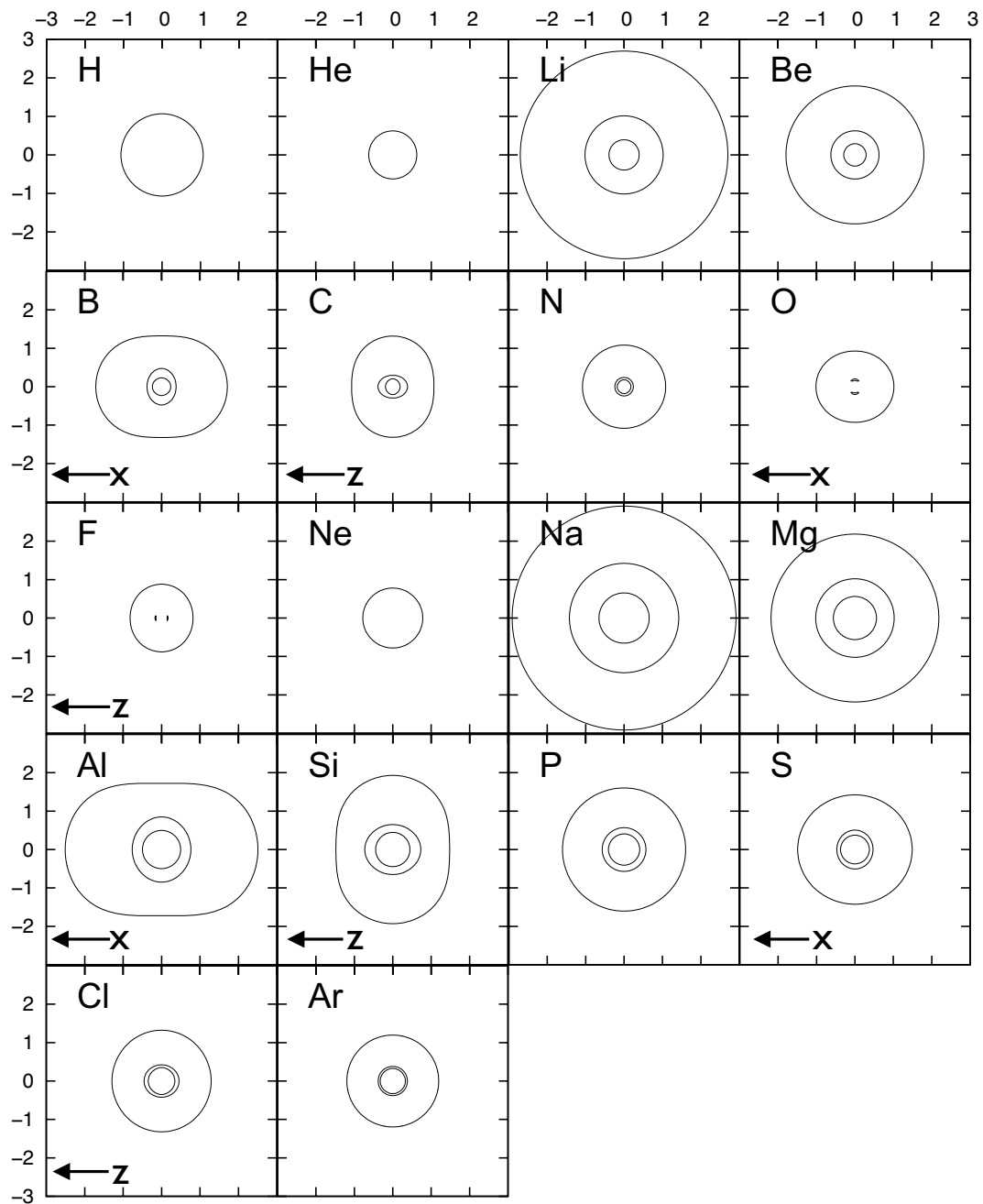


Fig. 2: Cross Sections of the electronic interfaces of the atoms. The horizontal axes coincide with the axial symmetry axes of the electronic interfaces. The units are in $\text{\AA}$.

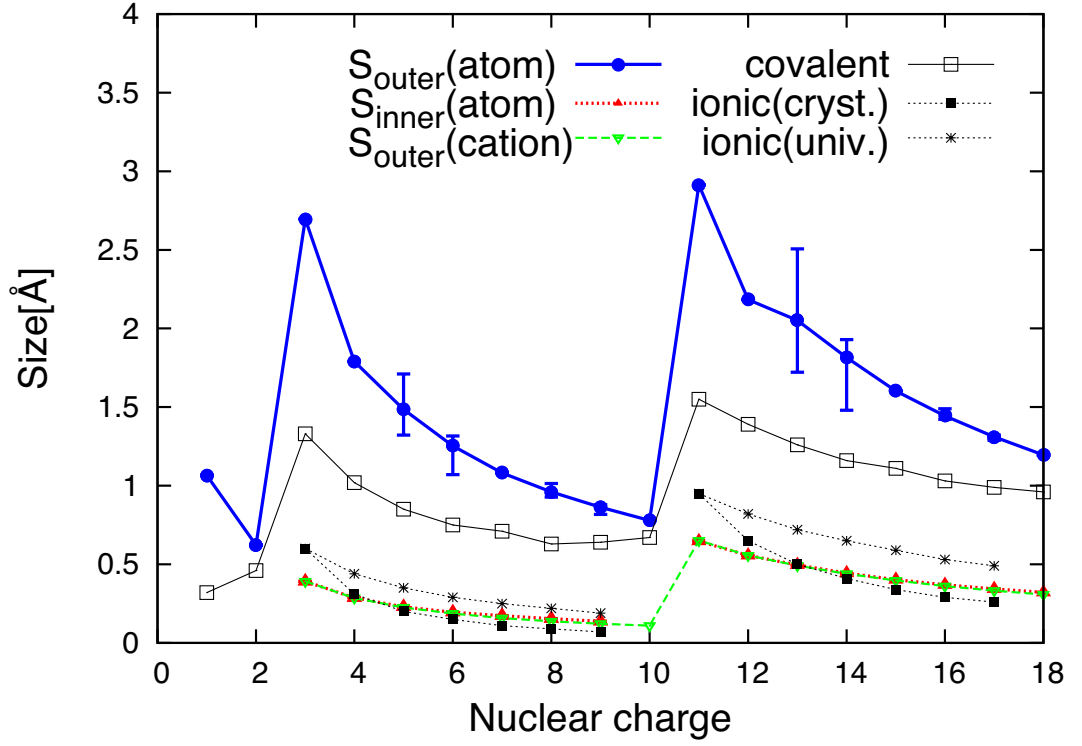


Fig. 3: The size of the electronic interfaces, which is defined in Sec. 1.3.2, are plotted for S_{outer} (blue solid line) and S_{inner} (red dotted line) of atoms, and S_{outer} of cations (green dashed line). Covalent radii from Ref. [8] (black thin solid line) and ionic radii from Ref. [9] (black thin dotted line) are plotted, too. As for the ionic radii, the crystal radii (line with filled-square) and univalent radii (line with asterisk) are plotted.

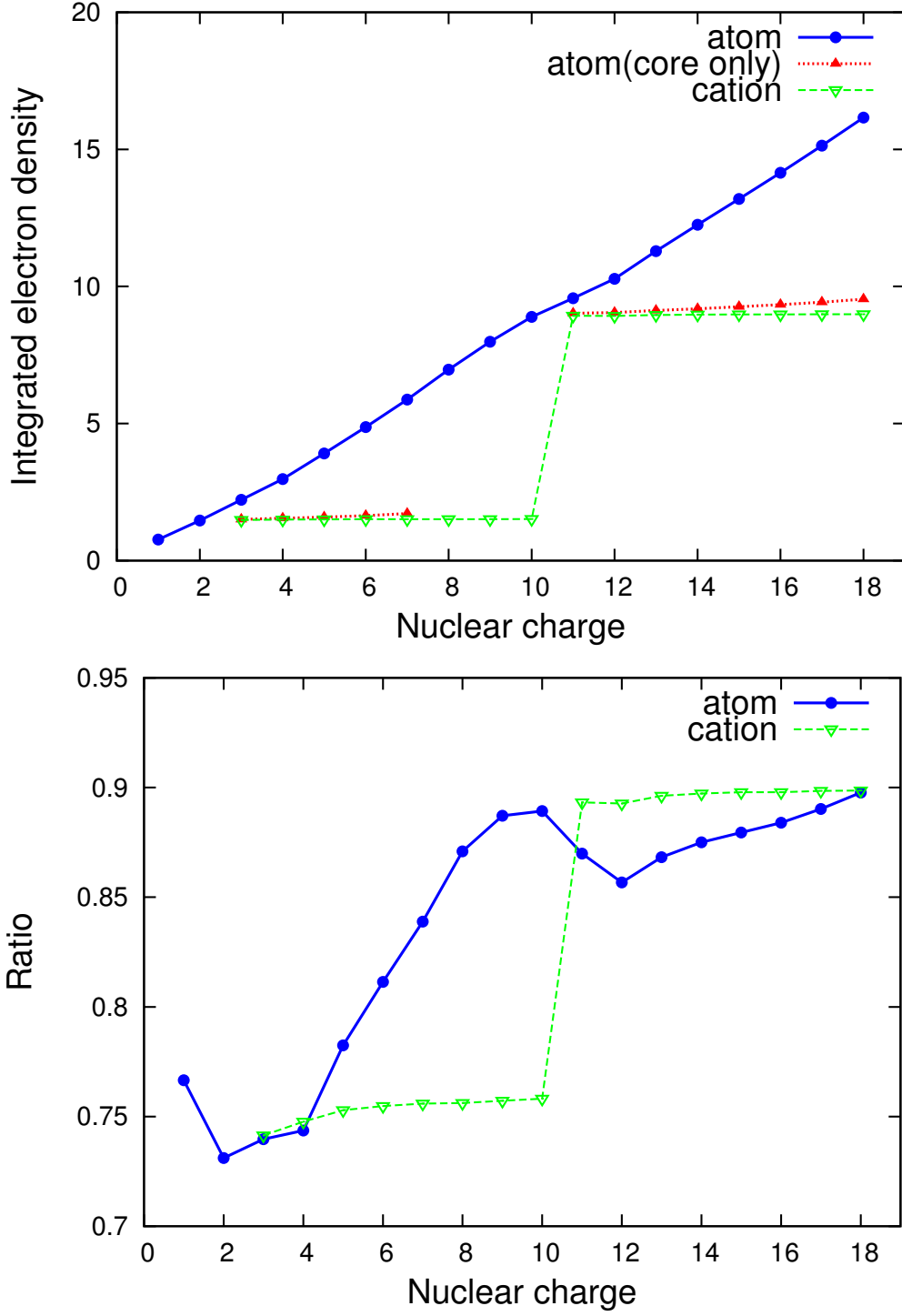


Fig. 4: In the upper panel, the electron density integrated over the total R_D of atoms (blue solid line), R_D of core region of atoms (red dotted line), and total R_D of cations (green dashed line), are plotted. In the lower panel, the ratios of the electron density integrated over R_D to the total electron number are plotted for atoms (blue solid line) and cations (green dashed line).

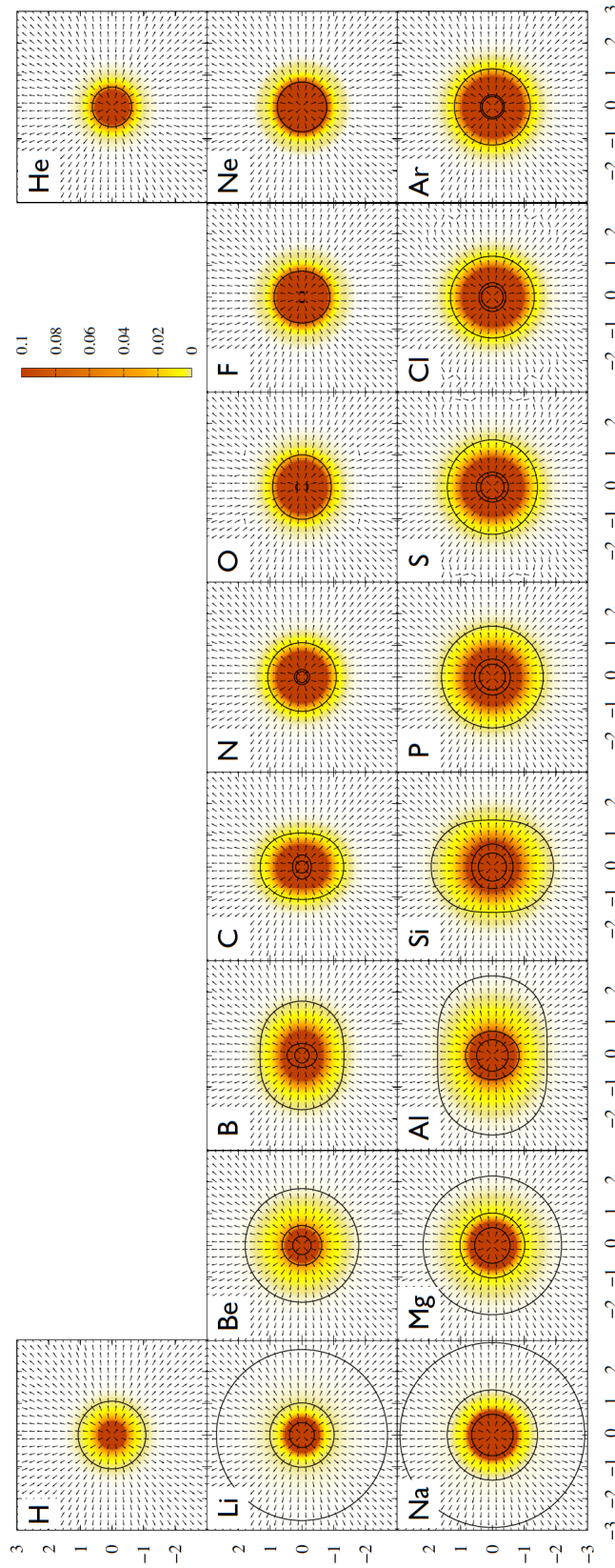


Fig. 5: The normalized tension density is plotted by the black arrows. Its norm is expressed by the color map. The black solid lines are the electronic interfaces as in Fig. 2.

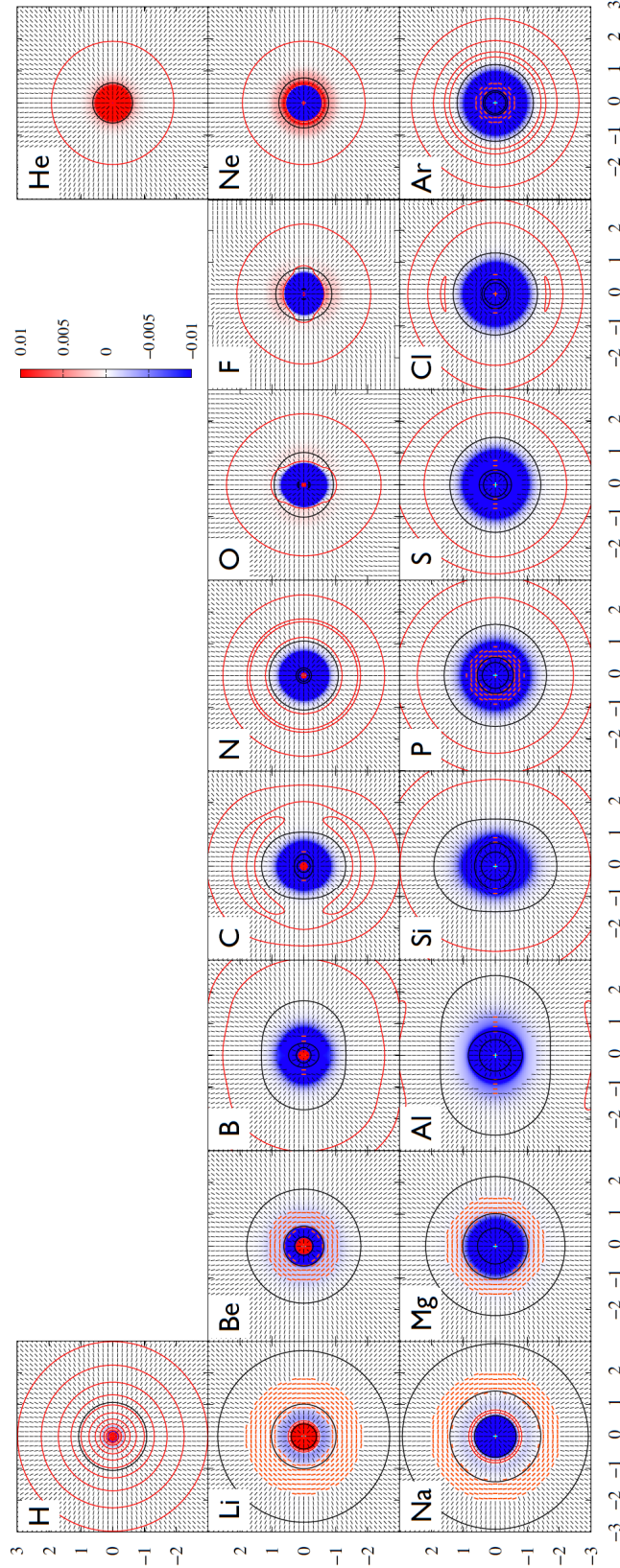


Fig. 6: The largest eigenvalue of the electronic stress tensor density (color map) and corresponding eigenvector (black rods) are plotted. The thick orange rods imply that the largest two eigenvalues are degenerated (see details for the text). Note that the red solid lines express the zero isosurfaces of the eigenvalue. The black solid lines are the electronic interfaces as in Fig. 2.

Supplementary Data

Contents

Fig. S1: The example of $S_{\text{outer}}(\text{atom})$, $S_{\text{inner}}(\text{atom})$ and $S_{\text{outer}}(\text{cation})$.

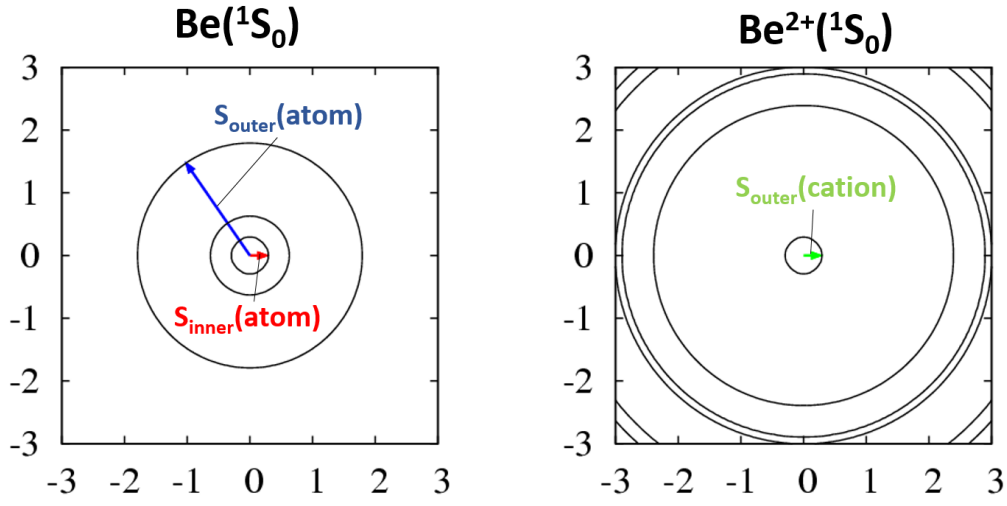


Fig. S1: $S_{\text{outer}}(\text{atom})$ and $S_{\text{inner}}(\text{atom})$ of $\text{Be}(^1S_0)$ and $S_{\text{outer}}(\text{cation})$ of $\text{Be}(^1S_0)$ are shown. We denote the outermost S of neutral atom as $S_{\text{outer}}(\text{atom})$, and the innermost S of neutral atom as $S_{\text{inner}}(\text{atom})$. Also, we denote the innermost S of cationized atom as $S_{\text{outer}}(\text{cation})$.

Chapter 2

2 Theoretical Study of Lithium Clusters by Electronic Stress Tensor

2.1 Introduction

The stress tensors in general are widely used for description of internal forces of matter in various fields of science such as mechanical engineering and material science. In quantum systems as well, the stress tensors have been investigated for many years, including one of the earliest quantum mechanics papers [7, 9–11, 14–22, 22–31]. As for the stress tensors in quantum mechanics context, we can find several different definitions and applications in the literature. For example, Ref. [19] and followers focus on the stress tensor which is associated with forces on nuclei. In contrast, the one we consider in this paper is the electronic stress tensor, which is associated with effects caused by internal forces acting on electrons in molecules, following Ref. [7]. This electronic stress tensor has been used to investigate chemical bonds and reactions and many interesting properties have been discovered [7, 9–11, 32–40].

We briefly review our past works on the electronic stress tensor which are closely related to this paper. In Ref. [9], it has been proposed that a covalent bond can be described by the eigenvalues and eigenvectors of the electronic stress tensor. In detail, the bonding region with covalency can be characterized and visualized by the “spindle structure”, where the largest eigenvalue of the electronic stress tensor is positive and the corresponding eigenvectors form a bundle of flow lines that connects nuclei. In Ref. [32], the eigenvalues of the electronic stress tensor of various homonuclear diatomic molecules have been investigated and all metals and metalloids molecules studied there exhibit the negative largest eigenvalue at the midpoint of the nuclei. Ref. [32] has mentioned that this negativity of the largest eigenvalue may be connected to the metallic nature of bonding but, at the same time, it has been known that the negative largest eigenvalue appears between a pair of atomic nuclei with very short distance such as the C-C bond in C_2H_2 [10, 32]. In Refs. [38] and [40], the Al_4 and Pd clusters have been investigated and we have shown “pseudo-spindle structure” [40] between metal nuclei. The pseudo-spindle structure is a negative eigenvalue version of the spindle structure and, more precisely, it is the region between two atoms where the largest eigenvalue of the electronic stress tensor is negative and corresponding eigenvectors forming a pattern which connects them. However, again, the pseudo-spindle structure is also seen in C_2H_2 [10, 39]. Since the pseudo-spindle structure is seen in many bonds between metal nuclei, it is tempting to associate it with a metallic bond, but it seems that the pseudo-spindle structure is not sufficient to capture the entire feature of a metallic bond.

In this paper, we would like to argue how we may describe a metallic bond using the electronic stress tensor. The conventional wisdom would say that it is not sensible to define “a metallic bond” because metal is something defined only for bulk with many electrons and ions. Our challenge is capturing some aspects of a metallic bond or metallicity of a chemical bond using the electronic stress tensor. As a starting point, we tackle this problem using small clusters of lithium, the simplest metal.

There are many studies on the nature of bonding in the Li clusters in the literature using such methods as by generalized valence-bond [33], electron localization function (ELF) [34, 35] and quantum theory of atoms in molecules (QTAIM) [36–38]. We would also like to see whether our stress tensor approach gives complementary views to these methods.

The structure of this paper is as follows. Sec. 2.2 briefly summarizes our analysis method of electronic structures using the electronic stress tensor. Sec. 4.3 shows our results of stress tensor analysis on the Li clusters. In Sec. 2.3.1, we discuss Li_2 . We also discuss H_2 and LiH for comparison. In Sec. 2.3.2, the Li clusters are analyzed and a method to use differential eigenvalues of the stress tensor is proposed. In Sec. 2.3.3, that method is applied to hydrocarbon molecules and its effectiveness is tested. Finally, Sec. 4.4 is devoted to our conclusion.

2.2 Theory and calculation methods

In this section, we summarize quantities and method we use for our electronic stress tensor analysis. Our stress tensor is based on the rigged quantum electrodynamics (QED) theory [7]. The rigged QED is the ordinary QED (the theory of photons and electrons) equipped with degrees of freedom of atomic nuclei in order to be used for atomic or molecular systems. Since this is a theory of quantum fields, there exist quantum operators defined at each point in spacetime. By using the equation of motion for operators of various physical quantities, many interesting operator relations have been found [7, 9–11].

The one related to the electronic stress tensor is the equation of motion of the kinetic momentum density operator. It turns out that the time derivative of the kinetic momentum density operator can be expressed by the sum of the two force operators: the tension density operator $\hat{\vec{\tau}}^S(\vec{r})$ and the Lorentz force density operator $\hat{\vec{L}}(\vec{r})$. $\hat{\vec{\tau}}^S(\vec{r})$ can be expressed by the divergence of some 3 by 3 tensor operator, which we call the stress tensor density operator $\hat{\vec{\tau}}^S(\vec{r})$. We obtain the quantum field theory version of the equilibrium equation of stress tensor by taking the expectation value of this equation of motion with respect to stationary electronic state of an atom or molecule (note that the expectation value of the time derivative of any operator with respect to stationary state is zero) as $0 = \vec{\tau}^S(\vec{r}) + \langle \hat{\vec{L}}(\vec{r}) \rangle$ or $0 = \sum_l \partial_l \tau^{Sk l}(\vec{r}) + \langle \hat{L}^k(\vec{r}) \rangle$ where $\{k, l\} = \{1, 2, 3\}$, $\langle \dots \rangle$ denotes the expectation value, $\vec{\tau}^S(\vec{r}) \equiv \langle \hat{\vec{\tau}}^S(\vec{r}) \rangle$ and $\tau^{Sk l}(\vec{r}) \equiv \langle \hat{\tau}^{Sk l}(\vec{r}) \rangle$.

The expectation values for the stress tensor density and tension density can be expressed as

$$\begin{aligned} \tau^{Sk l}(\vec{r}) = \frac{\hbar^2}{4m} \sum_i \nu_i & \left[\psi_i^*(\vec{r}) \frac{\partial^2 \psi_i(\vec{r})}{\partial x^k \partial x^l} - \frac{\partial \psi_i^*(\vec{r})}{\partial x^k} \frac{\partial \psi_i(\vec{r})}{\partial x^l} \right. \\ & \left. + \frac{\partial^2 \psi_i^*(\vec{r})}{\partial x^k \partial x^l} \psi_i(\vec{r}) - \frac{\partial \psi_i^*(\vec{r})}{\partial x^l} \frac{\partial \psi_i(\vec{r})}{\partial x^k} \right], \end{aligned} \quad (14)$$

$$\begin{aligned} \tau^{Sk}(\vec{r}) &= \sum_l \partial_l \tau^{Sk l}(\vec{r}) \\ &= \frac{\hbar^2}{4m} \sum_i \nu_i \left[\psi_i^*(\vec{r}) \frac{\partial \Delta \psi_i(\vec{r})}{\partial x^k} - \frac{\partial \psi_i^*(\vec{r})}{\partial x^k} \Delta \psi_i(\vec{r}) \right. \\ & \quad \left. + \frac{\partial \Delta \psi_i^*(\vec{r})}{\partial x^k} \psi_i(\vec{r}) - \Delta \psi_i^*(\vec{r}) \frac{\partial \psi_i(\vec{r})}{\partial x^k} \right], \end{aligned} \quad (15)$$

where $\{k, l\} = \{1, 2, 3\}$, m is the electron mass, $\psi_i(\vec{r})$ is the i th natural orbital and ν_i is its occupation number. Since the stress tensor is an Hermitian matrix, its eigenvalues are real and eigenvectors are orthogonal to each other. We denote the eigenvalues by λ_i ($i = 1, 2, 3$) with the ordering of $\lambda_3 \geq \lambda_2 \geq \lambda_1$.

The concept of ‘‘Lagrange point’’ is proposed in Ref. [32] and we use it as a point which can characterize a bond between two atoms. The Lagrange point $\vec{r}_L$ is the point where the tension density $\vec{\tau}^S(\vec{r})$ vanishes: $\tau^{Sk}(\vec{r}_L) = 0$. We report the eigenvalues of electronic stress tensor at this point in the following sections.

We also analyze electronic structure of molecules using kinetic energy density $n_T(\vec{r})$,

$$n_T(\vec{r}) = -\frac{\hbar^2}{4m} \sum_i \nu_i [\psi_i^*(\vec{r}) \Delta \psi_i(\vec{r}) + \Delta \psi_i^*(\vec{r}) \cdot \psi_i(\vec{r})], \quad (16)$$

which is defined in Ref. [7]. Note that our definition of the kinetic energy density is not positive-definite. Using this kinetic energy density, we can divide the whole space into three types of region: the electronic drop region R_D with $n_T(\vec{r}) > 0$, where classically allowed motion of electron is guaranteed and the electron density is amply accumulated; the electronic atmosphere region R_A with $n_T(\vec{r}) < 0$, where the motion of electron is classically forbidden and the electron density is dried up; and the electronic

interface S with $n_T(\vec{r}) = 0$, the boundary between R_D and R_A , which corresponds to a turning point. The S can give a clear image of the intrinsic shape of atoms and molecules and is therefore an important region in particular.

The electronic structures used in this paper are obtained by the Gaussian 09 [58] for cluster models and ABINIT [59, 60] for periodic models. We use Molecular Regional Density Functional Theory (MRDFT) package [42] to compute the quantities, Eqs. (39)-(40), introduced in this section. Some part of the visualization is done using PyMOL Molecular Viewer program [43].

2.3 Results and discussion

2.3.1 Li_2

In this section, we analyze the smallest Li cluster, Li_2 , by the electronic stress tensor. For comparison, we also show the results of stress tensor analysis of H_2 and LiH . The computation is performed by the coupled-cluster single-double (CCSD) method using the 6-311++G** basis set [45, 46].

Before we discuss Li_2 , we review how the chemical bond of the hydrogen molecule is expressed by the electronic stress tensor (Eq. (39)). In Fig. 1 (b), we plot the largest eigenvalue of the stress tensor and corresponding eigenvector on the plane including the internuclear axis. If the largest eigenvalue of the stress tensor is positive, it is called the tensile stress, and if negative, it is called the compressive stress. Namely, the sign of the largest eigenvalue tells whether electrons at a certain point in space exhibit tensile stress or compressive stress. The difference between tensile stress and compressive stress are described as follows. If we consider a fictitious plane at some point in atomic or molecular system, there are two ways that a part on one side of the plane acts on the other part of the plane. One is when electrons on one side of the plane is “pulled up” by the electron field on the other side. The other is when electrons on one side is “pushed back” by the electron field on the other side. The former corresponds to the tensile stress and the latter to the compressive stress. The direction of the eigenvector corresponds to the direction normal to the plane. In Fig. 1 (b), we can see that the region with positive eigenvalue spreads between the H atoms and, in that region, the eigenvectors form a bundle of flow lines that connects the H nuclei. Such a region is called “spindle structure” [9] and it is clearly seen in the figure. This means that electrons close to one H nucleus are pulled up by the electron field close to another H nucleus. Such a structure can be associated with the formation of the tight bonding and has a suitable directionality for a bond between two H nuclei. Thus, it is proposed that such positive eigenvalue region is the manifestation of the strong covalent bond [9].

We now turn to Li_2 , whose largest eigenvalue of the stress tensor and corresponding eigenvector is shown in Fig. 2 (b) in the same manner as H_2 . The striking difference is that there is a region with the negative largest eigenvalue between Li nuclei and there is no spindle structure. We do not even see a “pseudo-spindle structure” [40], the negative eigenvalue version of the spindle structure (*i.e.* the region with the eigenvectors forming a bundle of flow lines that connects two nuclei but with negative eigenvalues), which is frequently seen between metallic atoms [38–40]. This means that the electron field pushes back electrons in the neighboring regions with no solid directionality which can be considered as a bond axis. This is similar to the stress tensor of liquid. A liquid has the ability to flow. Liquid particles are loosely bound and they can move around one another freely. Such properties can be well associated with electrons in metal. In fact, coincidentally, metallic bonding is often described as an “electron sea” and the positively charged metal ions. It may be unusual to say Li_2 has purely a metallic bond with no trace of covalency but if we look at the electronic stress tensor, it is totally different from a covalent bond and certainly has a feature which can be called metallic. We will return to this point when we discuss larger Li clusters.

After seeing the difference between H_2 and Li_2 in terms of the electronic stress tensor, it may be interesting to see what the stress tensor of LiH look like. This is shown in Fig. 3 (b). It has both positive and negative regions between H and Li nuclei. The region close to H/Li has positive/negative eigenvalue. In the region very close to the internuclear axis, there is some flow of eigenvectors in the

direction of connecting the nuclei, but it is somewhat different from spindle or pseudo-spindle structures. Therefore, we can say that LiH has a bond with solid directionality like covalent bond of H_2 but there is a strong part nearby H and a weaker part nearby Li. It is tempting to associate this with an ionic bond, but we reserve conclusion until more examples are examined.

Since we have discussed the analogy between the stress tensors of Li_2 and liquid, it is important to investigate the other two eigenvalues. We plot all the three eigenvalues of the stress tensor for H_2 , Li_2 and LiH along the internuclear axes in Fig. 4. The bond length and the eigenvalues at the Lagrange point are summarized in Table 1. Let us first look at H_2 . As shown in Fig. 4 (a), around the midpoint of the two H nuclei, the largest eigenvalue (λ_3) is positive and the smaller eigenvalues (λ_1 and λ_2) are negative and degenerate. The absolute values of the three eigenvalues are $\mathcal{O}(0.1)$ and so are the differences between λ_3 and λ_1 or λ_2 . Fig. 4 (b) shows the case of Li_2 and we see that the three eigenvalues are all negative around the midpoint of the two Li nuclei. Two larger eigenvalues (λ_3 and λ_2) are degenerate and the smallest one (λ_1) is smaller than them by only $\mathcal{O}(10^{-4})$. Therefore, compared to the case of H_2 , the three eigenvalues of Li_2 can be regarded as degenerate. Such degeneracy in the eigenvalues of stress tensor, suggesting the lack of directionality, solidifies the analogy with liquid. Note that, in terms of the stress tensor, liquid is defined by the three eigenvalues which are negative and degenerate. This is in stark contrast with the case of H_2 , whose eigenvalue pattern indicates the strong directionality of the bond. The case of LiH is shown in Fig. 4 (c). The three eigenvalues are almost degenerate in the region close to Li and the region close to H has positive largest eigenvalue and two smaller eigenvalues are negative and degenerate. It is different from both Li_2 and H_2 and it looks like a mixture of Li_2 and H_2 . Such a feature could be a hint to consider how an ionic bond may be expressed by the electronic stress tensor, but, again, we need more examples.

So far, we have analyzed the molecules at the equilibrium distances and discussed their nature of bonding. We now try to extract more information by changing the internuclear distances. In particular, if we compute the stress tensors at very long distances, we can study the nature of bonding from the viewpoint of the bond formation.

The eigenvalues and eigenvectors of the stress tensor for H_2 , Li_2 and LiH at various internuclear distances are plotted in Figs. 1, 2 and 3. In the following discussion, the zero surface of the kinetic energy density (Sec. 2.2, Eq. (30)), the electronic interface S , plays an important role. As is explained in Sec. 2.2, S is the boundary between the electronic drop region R_D (where the electron density is accumulated) and the electronic atmosphere region R_A (where the electron density is dried up). In the figures, S is drawn by green dashed lines. To identify which side of S has positive or negative kinetic energy density (R_D or R_A), it is useful to remember R_D 's exist, naturally, around nuclei. When we look at the figures with very long internuclear distances, we see S exists around each nucleus, indicating that they do not form molecules and suggesting the existence of independent atoms. Moving to the figures with shorter internuclear distances, we see that S 's around nucleus get closer, merge and eventually form S for the molecules at the equilibrium distances. Incidentally, the state when S 's just begin to merge, namely touch each other, is called the "intrinsic electronic transition state" [7]. We denote the internuclear distance at this state by r^{TS} .

The notable fact is that, when the distance is so long that S 's are well separated (when practically considered as an infinite distance), we see the spindle structure at R_A between the two nuclei for all of H_2 , Li_2 and LiH (see Figs. 1 (d), 2 (h) and 3 (d) respectively). This means that electrons in R_D nearby nuclei are pulled up toward R_A through S , resulting in the formation of a Lewis electron pair. In other words, all the molecules are covalently bonded at the very long distances. In the case of H_2 , as shown in Fig. 1, the spindle structure continues to exist at shorter distances including $r_{HH}^{TS} = 2.20 \text{ \AA}$ and the equilibrium distance.

In the case of Li_2 , more interesting things happen. First, we observe that the spindle structure exist at the intrinsic electronic transition state ($r_{LiLi}^{TS} = 5.43 \text{ \AA}$, Fig. 2 (g)). Then, at $3.31 \text{ \AA}$, the positive eigenvalue region vanishes and the spindle structure turns into the pseudo-spindle structure. (Note that, at slightly longer distance of $3.36 \text{ \AA}$, the positive eigenvalue region vanishes on the internuclear axis while

positive areas remain away from the axis. Namely, between 3.36 Å and 3.31 Å, the positive region is not simply connected.) That pseudo-spindle structure is broken at 2.78 Å, at which three eigenvalues are degenerate (Fig. 5 (b)). At shorter distances, we see a negative region with no particular directionality such as to connect two nuclei, especially at the equilibrium distance. This is an example of what has been argued in Ref. [22]. When there are two distant Li atoms, the tensile stress (as is indicated by the spindle structure) pulls up electron in R_D to the adjacent R_A through S which separates them. The consequence is the formation of the long-range Lewis pair of electron. As the distant pair of Li atoms comes closer, the spindle structure disappears, indicating that the Lewis pair is unbound. This is considered to be a manifestation of metallicity.

In the case of LiH, at long distances, R_A between Li and H is characterized by the spindle structure as mentioned above and, in particular at $r_{\text{LiH}}^{\text{TS}} = 3.38$ Å. In Fig.3 (c), we see the contact point of the two interfaces is covered by the spindle structure. When the distance gets shorter, although the spindle structure is partly lost, the positive eigenvalue region remains around H. The negative eigenvalue region develops in the region close to Li but do not cover the whole space unlike the case of Li_2 . As for LiH, from the viewpoint of the electronic stress tensor, we may conclude that it has a bond which is neither covalent nor metallic. Whether we can categorize it as ionic or other bonding is an interesting question to ask and will be investigated in future.

2.3.2 Lithium clusters

The optimized structures for Li clusters, Li_n ($n = 3 \sim 8$) are shown in Fig. 6. In the figure, atoms are connected when the Lagrange point (Sec. 2.2) is found between them. These structures are obtained by re-optimizing the structures reported in Ref. [44]. We performed optimization with the three lowest multiplicities for each cluster and adopted the one with the lowest energy, which turned out to be singlet for clusters with even numbers of atoms and doublets for those with odd numbers. The computation is performed by the CCSD method using the 6-311++G** basis set [45, 46]. Although computational setups are slightly different, the obtained structures are basically consistent with Ref. [44]. As for Li_6 , Ref. [44] has reported the structure with D_{2h} symmetry while we have obtained the one with higher symmetry of D_{4h} , which is consistent with Ref. [47].

We first examine the largest eigenvalue of the stress tensor and corresponding eigenvector on the plane including three atoms in the Li clusters. They are plotted in Figs. 7 and 8. We omit equivalent bonds due to the structural symmetry. In these figures, every pair of atoms has a Lagrange point in between. We focus on the electronic drop regions (*i.e.* regions with positive kinetic energy density) between two atoms in each panel. The common feature is that they all have the largest eigenvalue which is negative. As for the eigenvectors, many regions do not show clear pattern such as to connect two atoms, just as the case of Li_2 . The regions with rather clear pseudo-spindle structures are found but not so common (the 1-2 bond in Li_6 (Fig. 7 (f)), the 1-2 bond in Li_7 (Fig. 8 (a)) and the 1-2 bond in Li_8 (Fig. 8 (c) or (d)).

From the discussion in Sec. 2.3.1, in order to characterize a chemical bond by the electronic stress tensor, it is important to know the pattern and degree of degeneracy of the three eigenvalues in addition to the sign of the largest eigenvalue. The three eigenvalues of stress tensor at the Lagrange points are summarized in Table 2. From the table, we can reconfirm that the eigenvalues are all negative. In addition, we see that the three eigenvalues are close to each other as is the case of Li_2 at least at the Lagrange points.

In order to quantify the degeneracy pattern more clearly, we propose to use following differential eigenvalues.

$$\lambda_{D32} \equiv \lambda_3 - \lambda_2, \quad (17)$$

$$\lambda_{D21} \equiv \lambda_2 - \lambda_1. \quad (18)$$

Since our convention is $\lambda_3 \geq \lambda_2 \geq \lambda_1$, λ_{D32} and λ_{D21} are positive. For example, at the Lagrange point,

$(\lambda_{D32}, \lambda_{D21}) = (0.394, 0)$ for H_2 , $(0, 2.37 \times 10^{-4})$ for Li_2 and $(8.52 \times 10^{-3}, 0)$ for LiH . In Fig. 9 (a), we plot $(\lambda_{D32}, \lambda_{D21})$ at the Lagrange points for the Li clusters. It is shown that the Li clusters have very small values of λ_{D32} and λ_{D21} , the same order as that of λ_{D21} of Li_2 and much smaller than λ_{D32} of H_2 . Thus, we can consider three eigenvalues of the Li clusters are almost degenerate, meaning the high degree of isotropy (low degree of directionality) of the electronic stress tensor. Together with their negativity, the stress tensor of the Li clusters are just like that of liquid. As we have mentioned in Sec. 2.3.1, electrons in metal are readily associated with particles in liquid. By turning this argument around, we may try to consider that negativity and degeneracy of the eigenvalues of the electronic stress tensor characterize and quantify some aspects of the metallic nature of chemical bonding.

To support the validity of this idea, we here show some data of very small Na clusters, Na_n ($n = 2 \sim 4$). The electronic structures are obtained by the same computational setups as the Li clusters. We performed geometrical optimization starting from the structures reported in Refs. [47, 48]. The most stable structures turned out to be singlet for clusters with even numbers of atoms and doublets for those with odd numbers. As for the symmetry of those structures, Na_3 and Na_4 are found to have C_{2v} and D_{2h} symmetry. The results of the electronic stress tensor analysis are summarized in Table 3. From the data in the table, we readily see that the eigenvalues are all negative and almost degenerate just as the case of Li clusters.

As another way to test this idea, we analyze the electronic stress tensor of periodic models for bulk Li and Na. The body-centered cubic structure is adopted for both Li and Na with the lattice constants taken to be $3.491 \text{ \AA}$ and $4.225 \text{ \AA}$ respectively. We use the norm-conserving pseudopotentials of Troullier-Martins type [56] and the generalized-gradient approximation method by Perdew-Burke-Ernzerhof [57] for density functional exchange-correlation interactions. Kinetic energy cutoff of plane-wave expansion (k-point) is taken as 40.0 hartree ($2 \times 2 \times 2$ k-point set). We compute the electronic stress tensor at the midpoint of two nearest neighborhood atoms. We obtain $\lambda_3 = -0.468 \times 10^{-3}$ and $\lambda_2 = \lambda_1 = -0.716 \times 10^{-3}$ for Li, and $\lambda_3 = \lambda_2 = -0.253 \times 10^{-3}$ and $\lambda_1 = -0.293 \times 10^{-3}$ for Na. As for the differential eigenvalues, $(\lambda_{D32}, \lambda_{D21}) = (2.48 \times 10^{-4}, 0)$ for Li and $(0, 3.95 \times 10^{-5})$ for Na. These results show that the negativity and degeneracy of the eigenvalues of the electronic stress tensor are found in the bulk systems too, and the degrees of negativity and degeneracy are not different from the clusters.

Here, some comments are in order as for comparison with the studies in the literature. As shown just above, from the viewpoint of the electronic stress tensor, the chemical bonds in the small Li clusters look similar to the bulk Li. They possess compressive stress (negative eigenvalues) with no particular directionality (almost degenerate eigenvalues) like liquid, which can be considered as one of the important features of metal. Interesting thing is that this is even so with Li_2 . Past studies like Refs. [33, 34] show multi-center bonds are ubiquitous features of the Li clusters. In particular, Ref. [34] argues that the metallic phase of Li is characterized by multi-center bonds and very gentle variation of ELF across space. From this viewpoint, since Li_2 is not multi-centered by definition, Li_2 does not have a common feature with bulk Li or the other Li clusters. This point is in stark contrast with the stress tensor viewpoint. We note that, in Ref. [36, 37], where Li_2 is studied in the framework of QTAIM, Li_2 is viewed as a system that two Li atoms are bonded to a pseudo atom (the central nonnuclear attractor) and electrons at the central regions are associated with those “partially behave as mobile metallic electron”. The viewpoint of the stress tensor is closer to one of QTAIM in a sense that Li_2 already exhibits some aspects of chemical bonding which characterizes bulk Li.

2.3.3 Comparison with other molecules

In this section, we analyze hydrocarbon molecules and compare with the Li clusters, especially regarding the negativity and degeneracy of the eigenvalues of the electronic stress tensor. Ref. [33] has studied hydrocarbon molecules using the electronic stress tensor. We use similar set of molecules but not exactly the same one. The complete list of structures of our set which consists of 48 molecules is shown in the

supplementary material (Fig. S1 [51]). The structures of these hydrocarbon molecules are obtained by optimization using the density functional theory (DFT) method with B3LYP [45, 52] as a functional and the 6-311++G** basis set.

As for the electronic stress tensor analysis, we repeat the same analyses which has been carried out for the Li clusters in the previous section. We begin by investigating the largest eigenvalue of stress tensor. We find that most of the bonds have positive largest eigenvalues. Negative largest eigenvalues are found in some of the triple C-C bonds, as is mentioned in Sec. 4.1. In our data set, the triple C-C bonds in C_2HX with X being H, CH_3 , C_2H_5 , NH_2 , OH, F, Cl and Br have the largest eigenvalues which are negative and whose absolute values are $\mathcal{O}(10^{-3})$ or less (the three eigenvalues for these bonds against the bond lengths are plotted in Fig. S2 in the supplementary material [51]). It is known that this negativity of the largest eigenvalue in these triple bonds can be attributed to the very short bond and not to metallicity [10, 33, 39]. The pattern of degeneracy of three eigenvalues of the electronic stress tensor is very different from that of the Li clusters. In the hydrocarbon molecules, the smaller two eigenvalues are degenerate, $\lambda_1 \approx \lambda_2$, and λ_3 has much larger values which are mostly positive. Thus, if we only focus on the largest eigenvalue, these triple C-C bonds and the bonds in the Li clusters look similar. However, by looking at the other two eigenvalues, we can clearly distinguish them.

As is done in the previous section, we compute the differential eigenvalues λ_{D32} and λ_{D21} at the Lagrange points in the hydrocarbons. This is plotted in Fig. 9 (b) and we see that λ_{D32} is much larger than λ_{D21} . It means that the smaller two eigenvalues are relatively degenerate and the largest one is much larger than those two. This distribution pattern is quite different from that of the Li clusters shown in Fig. 9 (a). Let us summarize our results using the differential eigenvalues. The Li clusters are characterized by $\lambda_{D32} \ll 1$ and $\lambda_{D21} \ll 1$ whereas the hydrocarbon molecules $\lambda_{D32} \gg \lambda_{D21}$ and $\lambda_{D21} \ll 1$. In particular, $\lambda_{D32}(Li_n) \approx \lambda_{D21}(Li_n) \ll \lambda_{D32}(h/c)$. This means that the electronic stress tensor between atom pairs in the hydrocarbon molecules shows directionality while it does not show much directionality in the case of the Li clusters.

In summary of this section, first of all, we find that most of the hydrocarbon molecules are different from the Li clusters in a sense that the largest eigenvalue of the stress tensor is positive. Although some of the triple C-C bonds have the largest eigenvalue which is negative, they do not look like those of the Li clusters due to the non-degeneracy of the eigenvalues. There is no hydrocarbon molecule which has the electronic stress tensor like that of liquid, at least in our hydrocarbon molecule set. Thus, this results are not inconsistent with the idea proposed in the last section that negativity and degeneracy of the eigenvalues of the electronic stress tensor may characterize and quantify some aspects of the metallicity of chemical bonding.

2.4 Conclusion

In this paper, we have studied the electronic structure of small lithium clusters Li_n ($n = 2 \sim 8$) using the electronic stress tensor. We have found that the degeneracy pattern of the three eigenvalues λ_i ($i = 1, 2, 3$) ($\lambda_3 \geq \lambda_2 \geq \lambda_1$) of the electronic stress tensor at the Lagrange points of the Li clusters is very much different from that of the hydrocarbon molecules, which are covalently bonded. Namely, the three eigenvalues of the Li clusters have almost same values while the hydrocarbon molecules have the largest eigenvalue much larger than the second largest eigenvalue, which has similar value to the smallest eigenvalue. The former degeneracy pattern indicates that the bonds are not directional while the latter indicates the clear directionality of the bonds. The negativity of the largest eigenvalue is not unique feature of the Li clusters (some of the C-C triple bonds exhibit the negative largest eigenvalue) but this degeneracy is characteristic to Li. We can consider that such difference in the degeneracy pattern reflects the metallic nature of bonding of the Li clusters and the covalent nature of bonding of the hydrocarbon molecules. Note that the negativity and degeneracy of the stress tensor, which is the property of the liquid, is readily associated with the tradition that the metal can be viewed as “electron sea”.

To describe the degeneracy pattern of the eigenvalues in a compact manner, we have proposed to use the differential eigenvalues: $\lambda_{D32} = \lambda_3 - \lambda_2$ and $\lambda_{D21} = \lambda_2 - \lambda_1$. By using them, the degeneracy patterns of the eigenvalues can be summarized as $\lambda_{D32}(\text{Li}_n) \approx \lambda_{D21}(\text{Li}_n) \ll \lambda_{D32}(\text{h/c}) \sim \mathcal{O}(0.1)$. It is of great interest whether this relation can be extended as $\lambda_{D32}(\text{metallic}) \approx \lambda_{D21}(\text{metallic}) \ll \lambda_{D32}(\text{covalent})$ in general. In this paper, we have only examined the Li clusters with limited numbers of atoms. It is important to check this relation with larger Li clusters and also with other metal clusters. Then, the role of the electronic stress tensor in describing the metallicity would be elucidated and more detailed classification among the “metallic bond” would be possible.

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Table 1: The bond length and the eigenvalues λ_i ($i = 1, 2, 3$) of the electronic stress tensor at the Lagrange point for H_2 , Li_2 and LiH .

Bond	length[Å]	λ_3	λ_2	λ_1
H_2	0.743	0.175	-0.219	-0.219
Li_2	2.692	-1.025×10^{-3}	-1.025×10^{-3}	-1.262×10^{-3}
LiH	1.601	-4.954×10^{-3}	-1.347×10^{-2}	-1.347×10^{-2}

Table 2: The bond length and the eigenvalues λ_i ($i = 1, 2, 3$) of the electronic stress tensor at the Lagrange point for bonds in the Li clusters. The numbers in the second column correspond to those labelled in Fig. 6.

Cluster	bond	length [Å]	$\lambda_3(\times 10^3)$	$\lambda_2(\times 10^3)$	$\lambda_1(\times 10^3)$
Li_3	1-2	2.782	-0.900	-0.993	-1.054
	1-3	3.275	-0.271	-0.463	-0.781
Li_4	1-2	2.667	-0.793	-0.919	-1.240
	1-3	3.010	-0.498	-0.763	-0.981
Li_5	1-2	2.929	-0.516	-0.708	-1.152
	1-3	2.927	-0.519	-0.715	-1.163
	1-4	3.085	-0.494	-0.746	-0.836
	2-3	2.618	-1.139	-1.157	-1.348
	2-4	3.028	-0.494	-0.789	-1.016
	3-4	3.027	-0.494	-0.790	-1.016
Li_6	1-2	2.640	-1.004	-1.410	-1.410
	1-3	2.849	-0.600	-0.924	-1.198
Li_7	1-2	2.820	-0.684	-1.064	-1.064
	1-3	2.974	-0.572	-0.861	-0.861
	3-4	3.078	-0.465	-0.636	-0.787
Li_8	1-2	2.926	-0.584	-0.826	-0.918
	1-5	3.040	-0.474	-0.719	-0.814

Table 3: The bond length and the eigenvalues λ_i ($i = 1, 2, 3$) of the electronic stress tensor at the Lagrange point for bonds in the Na clusters. Since Na_3 and Na_4 respectively have C_{2v} and D_{2h} symmetry groups, which are same as the Li cluster case, one may refer to Fig. 6 for the numbers in the second column. Note that we do not find the Lagrange point between the atoms 1 and 3 (with the separation of 4.371 Å) of Na_3 .

Cluster	bond	length [Å]	$\lambda_3(\times 10^3)$	$\lambda_2(\times 10^3)$	$\lambda_1(\times 10^3)$
Na_2	1-2	3.162	-0.532	-0.532	-0.752
Na_3	1-2	3.316	-0.430	-0.444	-0.475
Na_4	1-2	3.232	-0.418	-0.453	-0.514
	1-3	3.578	-0.264	-0.334	-0.424

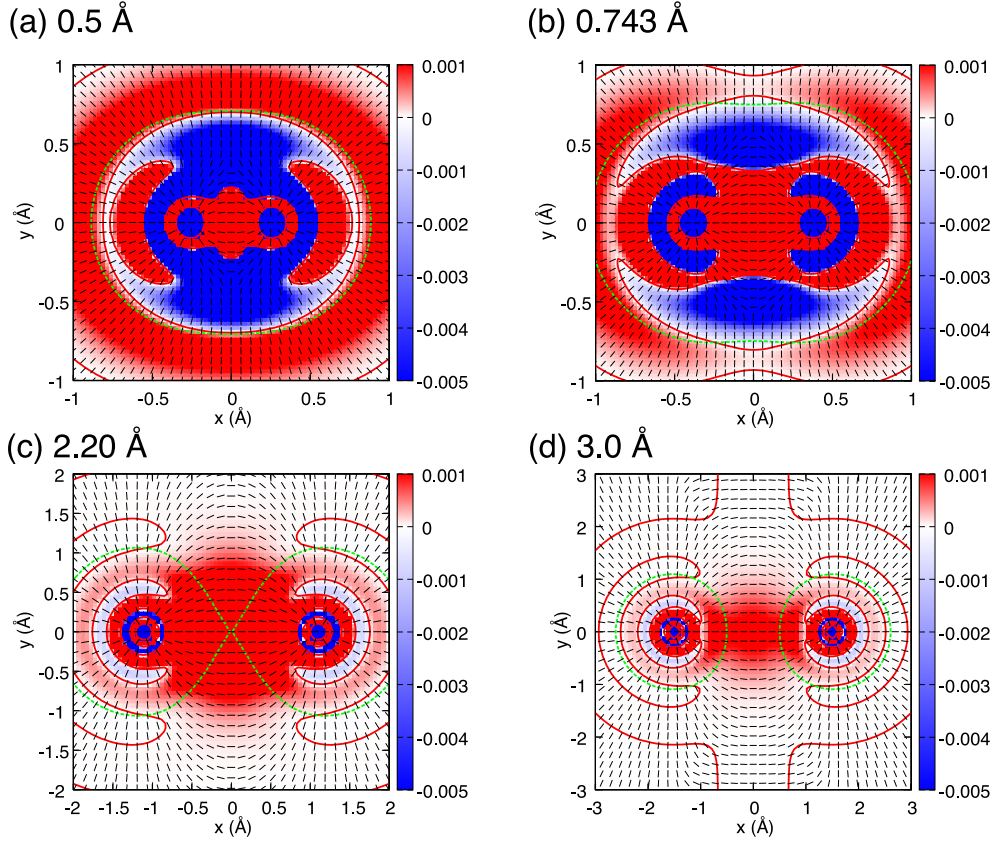


Fig. 1: The largest eigenvalue of the stress tensor (color map) and corresponding eigenvector (black rods) of H_2 at various internuclear distances: (a) 0.5 Å, (b) 0.743 Å (equilibrium distance), (c) 2.20 Å (intrinsic electronic transition state) and (d) 3.0 Å. As for the eigenvectors, the projection on this plane is plotted. The red solid line denotes a contour where the eigenvalue is zero. The green dashed line denotes a contour where the kinetic energy density is zero (electronic interface).

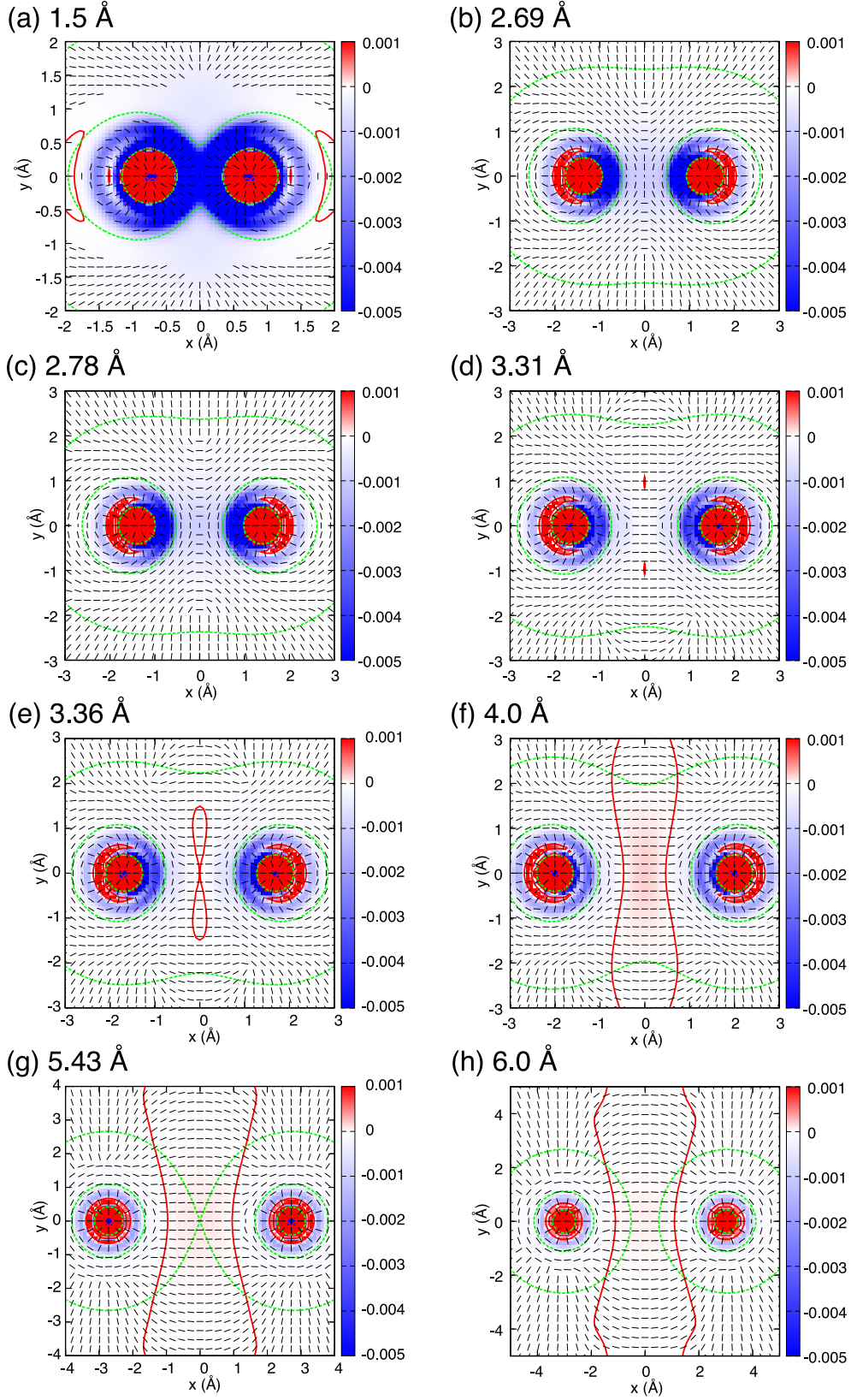


Fig. 2: The largest eigenvalue of the stress tensor and corresponding eigenvector of Li_2 at various internuclear distances (a) 1.5 $\text{\AA}$, (b) 2.69 $\text{\AA}$ (equilibrium distance), (c) 2.78 $\text{\AA}$, (d) 3.31 $\text{\AA}$, (e) 3.36 $\text{\AA}$, (f) 4.0 $\text{\AA}$, (g) 5.43 $\text{\AA}$ (intrinsic electronic transition state) and (h) 6.0 $\text{\AA}$. Plotted in the same manner as Fig. 1.

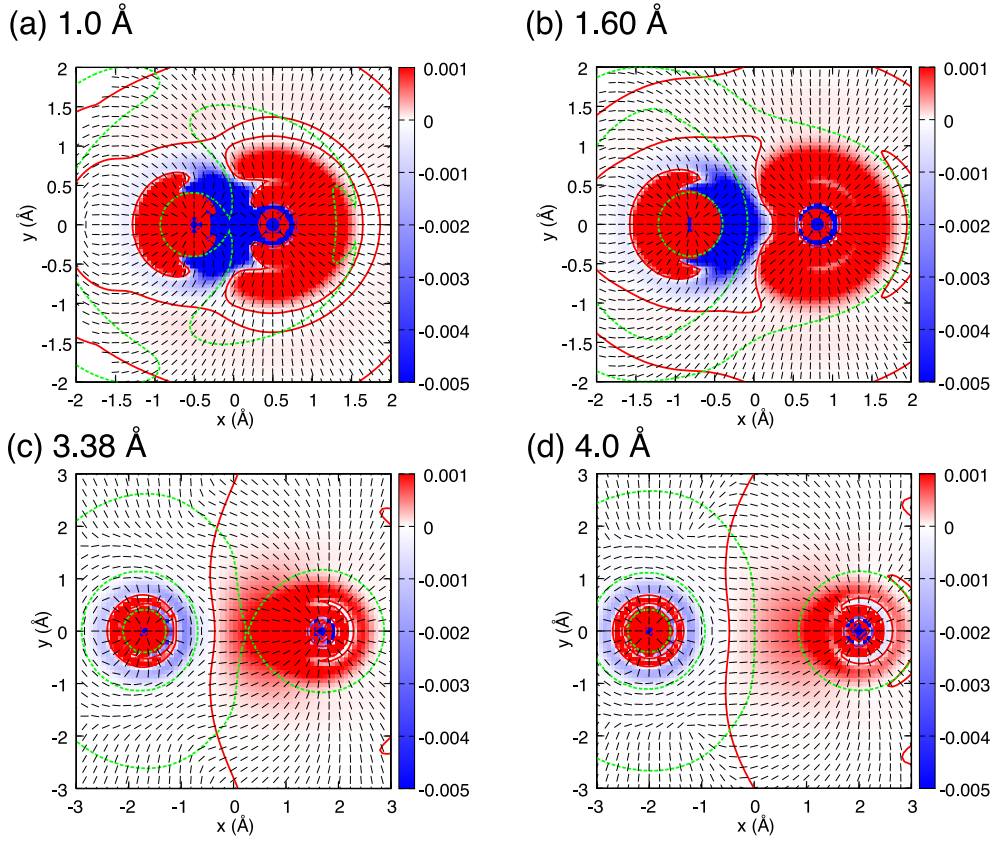


Fig. 3: The largest eigenvalue of the stress tensor and corresponding eigenvector of LiH at various inter-nuclear distances: (a) 1.0 Å, (b) 1.61 Å (equilibrium distance), (c) 3.38 Å (intrinsic electronic transition state) and (d) 4.0 Å. Plotted in the same manner as Fig. 1.

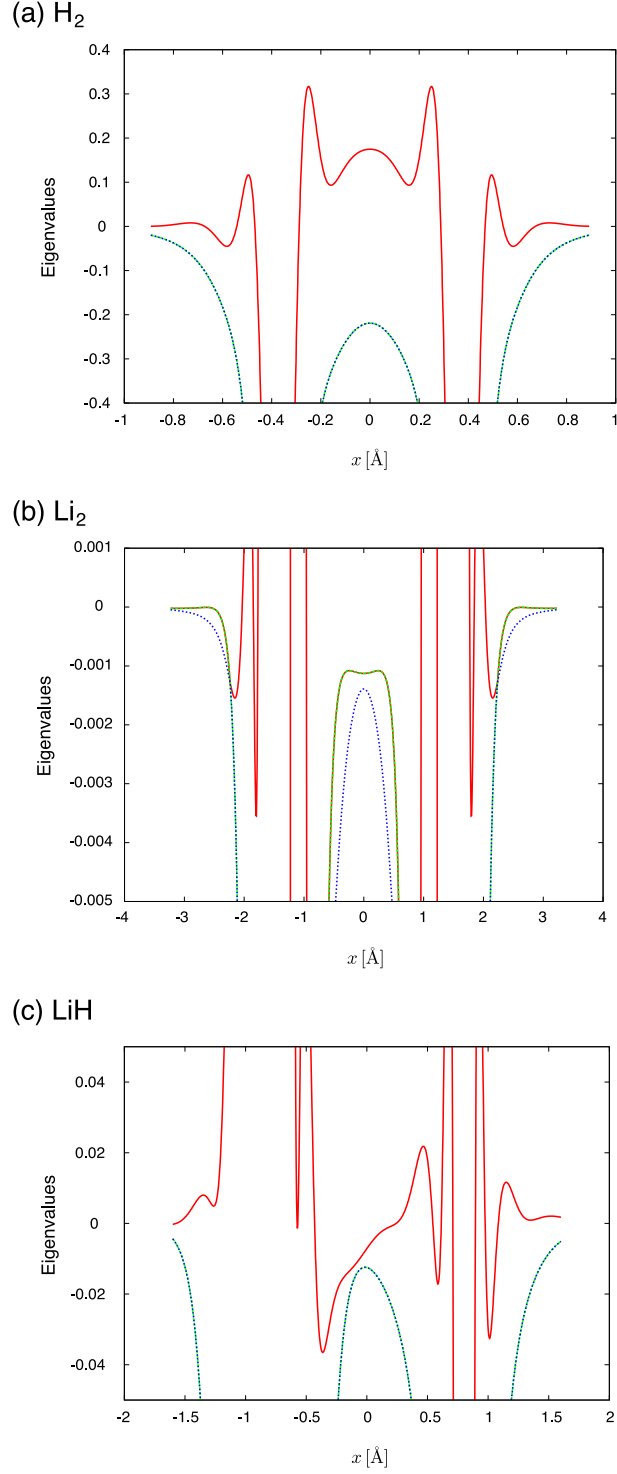


Fig. 4: Three eigenvalues of the stress tensor for H_2 (panel (a)), Li_2 (panel (b)) and LiH (panel (c)) along the internuclear axis. The red solid lines are for the largest eigenvalue (λ_3), the green dashed lines are for the second largest eigenvalue (λ_2) and the blue dotted lines are for the smallest eigenvalue (λ_1). The internuclear distances are set to be their equilibrium distances. The origin of the abscissa corresponds to the midpoint of two nuclei.

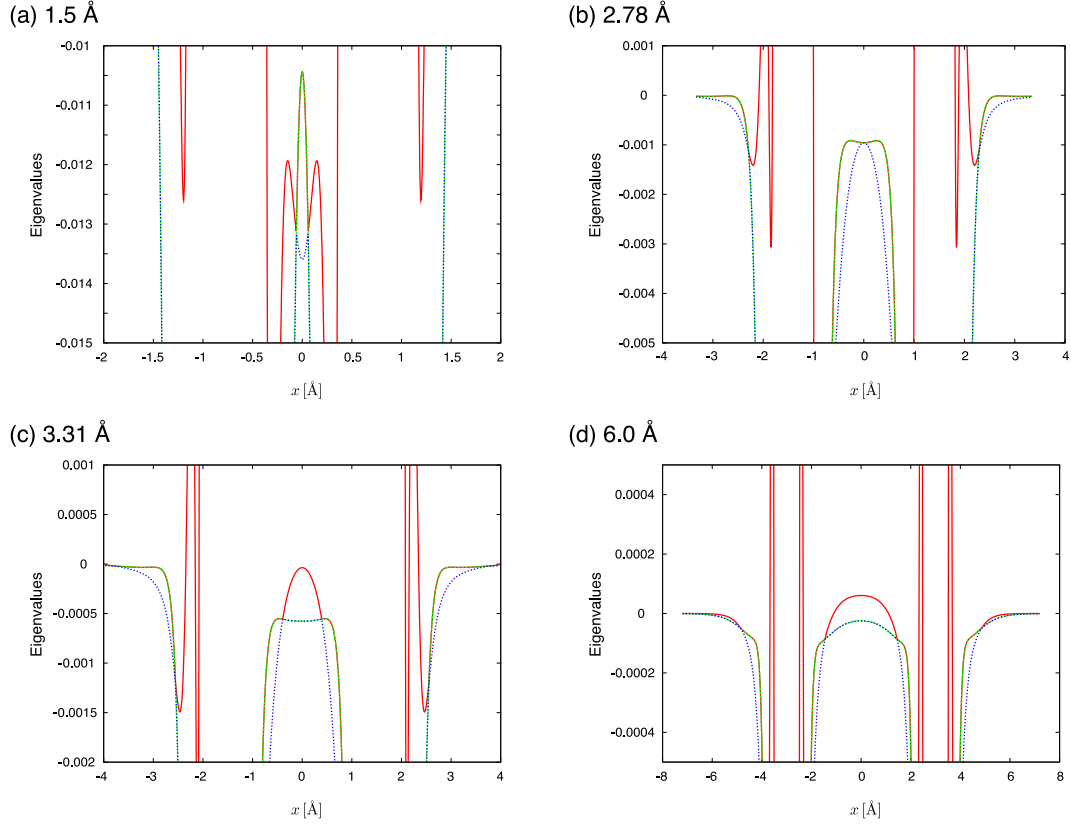
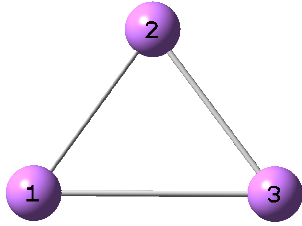
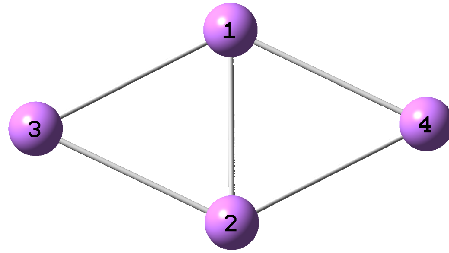


Fig. 5: Three eigenvalues of the stress tensor for Li_2 along the internuclear axis at various internuclear distances: (a) 1.5 Å, (b) 2.78 Å, (c) 3.31 Å and (d) 6.0 Å. The red solid lines are for the largest eigenvalue (λ_3), the green dashed lines are for the second largest eigenvalue (λ_2) and the blue dotted lines are for the smallest eigenvalue (λ_1).

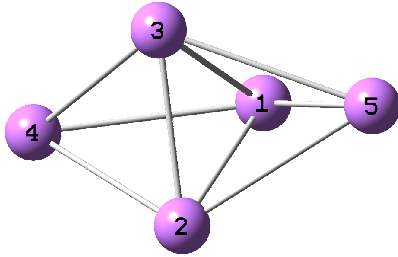
(a) Li_3 (C_{2v})



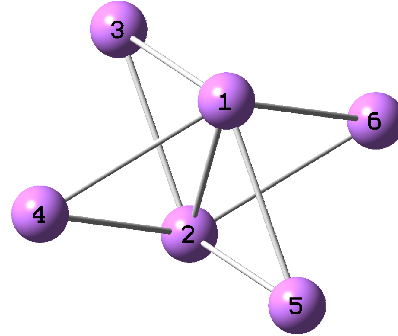
(b) Li_4 (D_{2h})



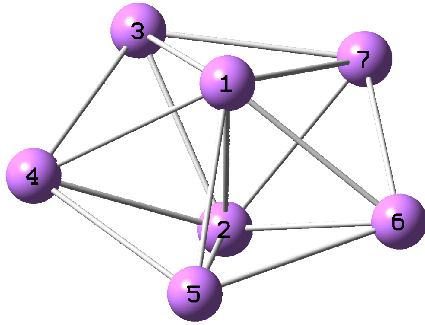
(c) Li_5 (C_s)



(d) Li_6 (D_{4h})



(e) Li_7 (D_{5h})



(f) Li_8 (T_d)

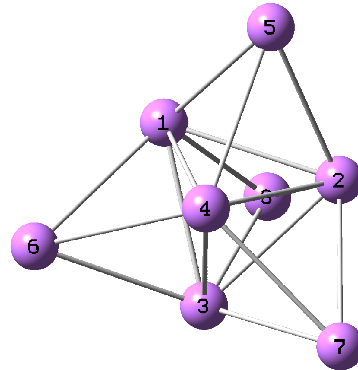


Fig. 6: Optimized structures of Li clusters: (a) Li_3 (C_{2v}), (b) Li_4 (D_{2h}), (c) Li_5 (C_s), (d) Li_6 (D_{4h}), (e) Li_7 (D_{5h}) and (f) Li_8 (T_d). The bonds are drawn at which the Lagrange points are found.

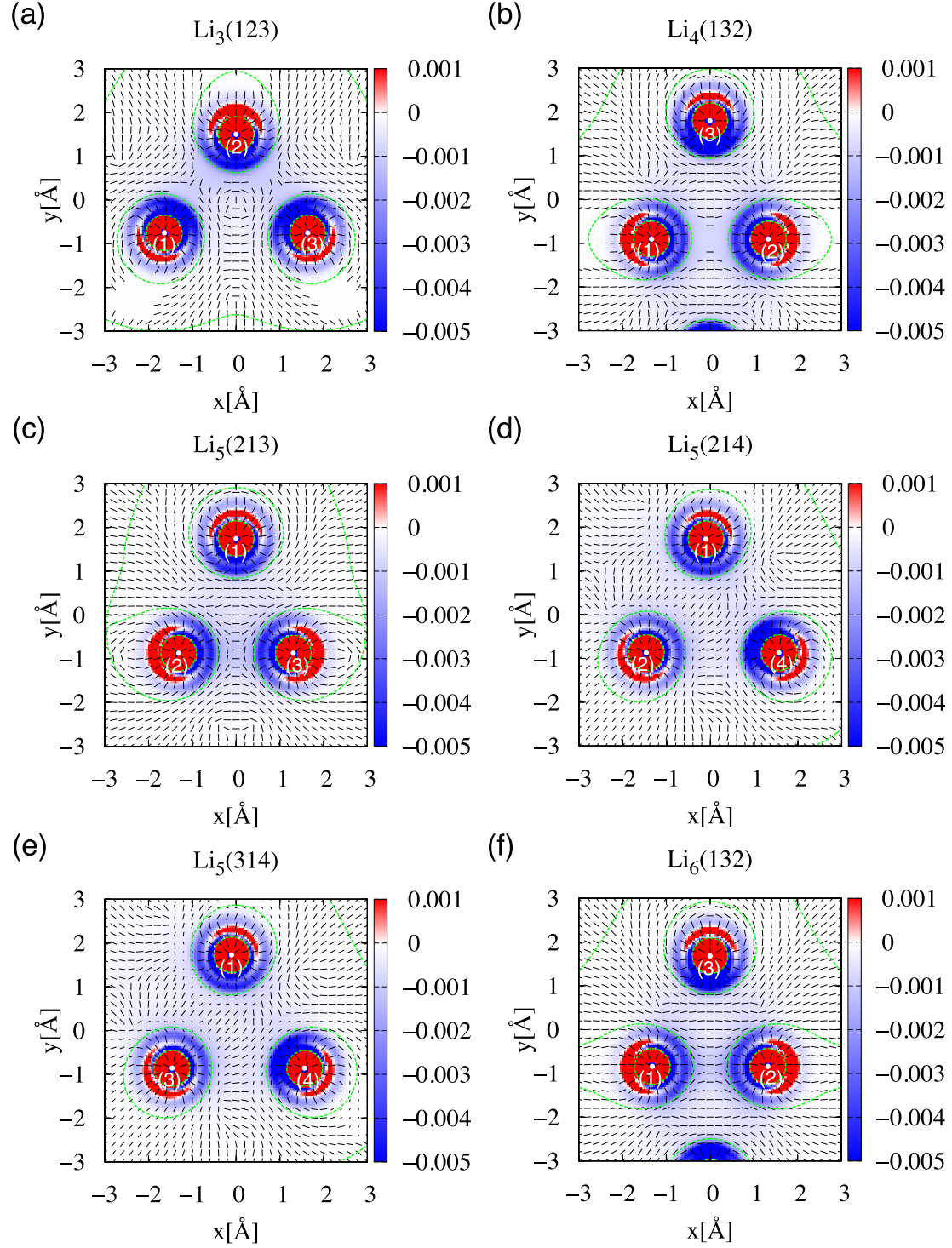


Fig. 7: The largest eigenvalue of the stress tensor (color map) and corresponding eigenvector for Li clusters Li_n ($n = 3 \sim 6$). Plotted in similar manner to Fig. 1. The filled circles denote the positions of the atoms and the numbers in parentheses correspond to those labelled in Fig. 6.

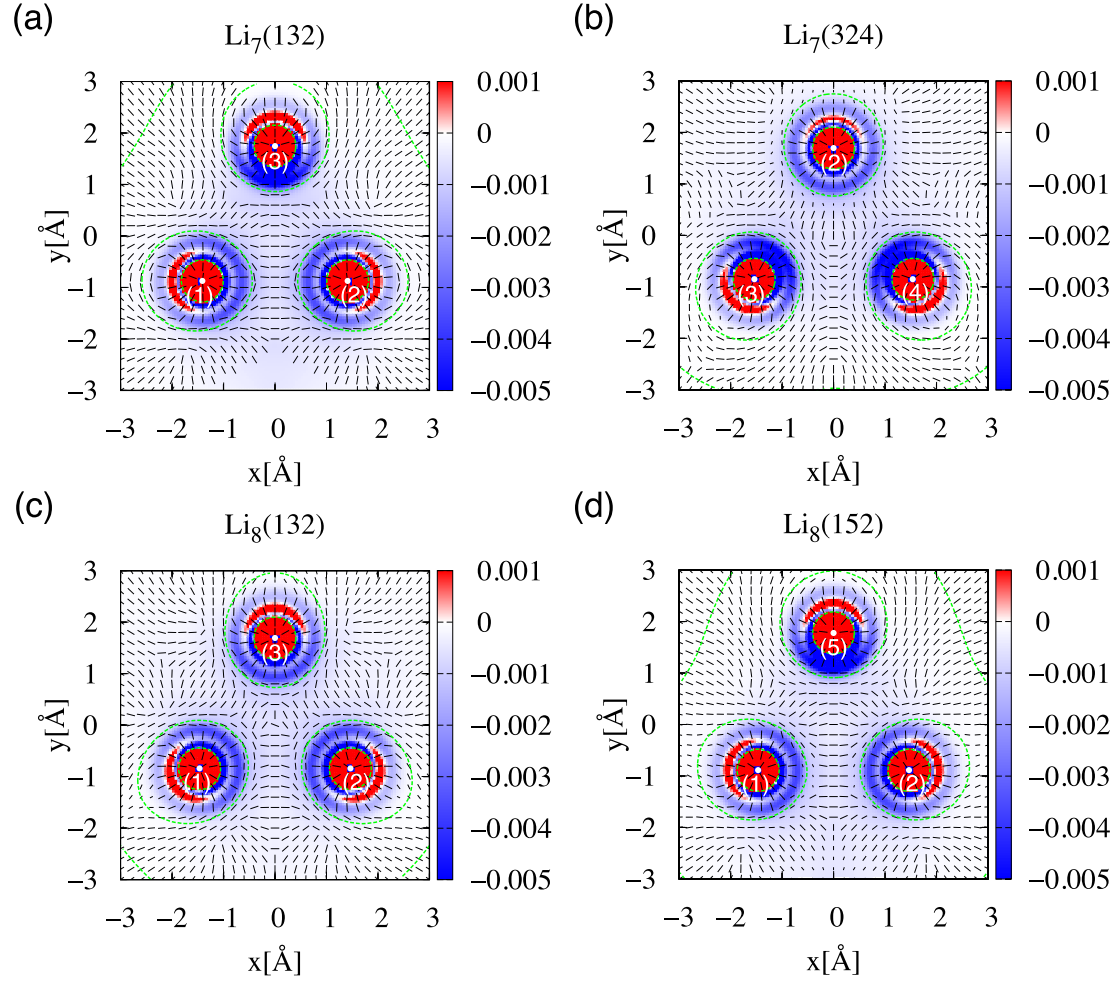
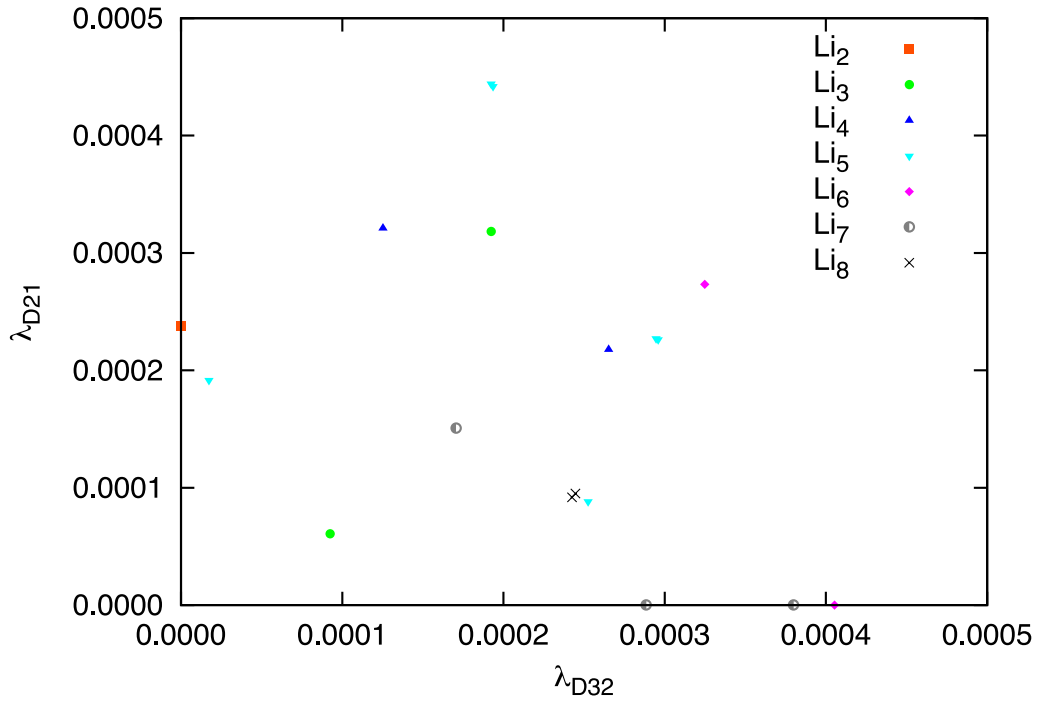


Fig. 8: The largest eigenvalue of the stress tensor (color map) and corresponding eigenvector for Li clusters Li_n ($n = 7 \sim 8$). The optimized structures are used. Plotted in similar manner to Fig. 7.

(a)



(b)

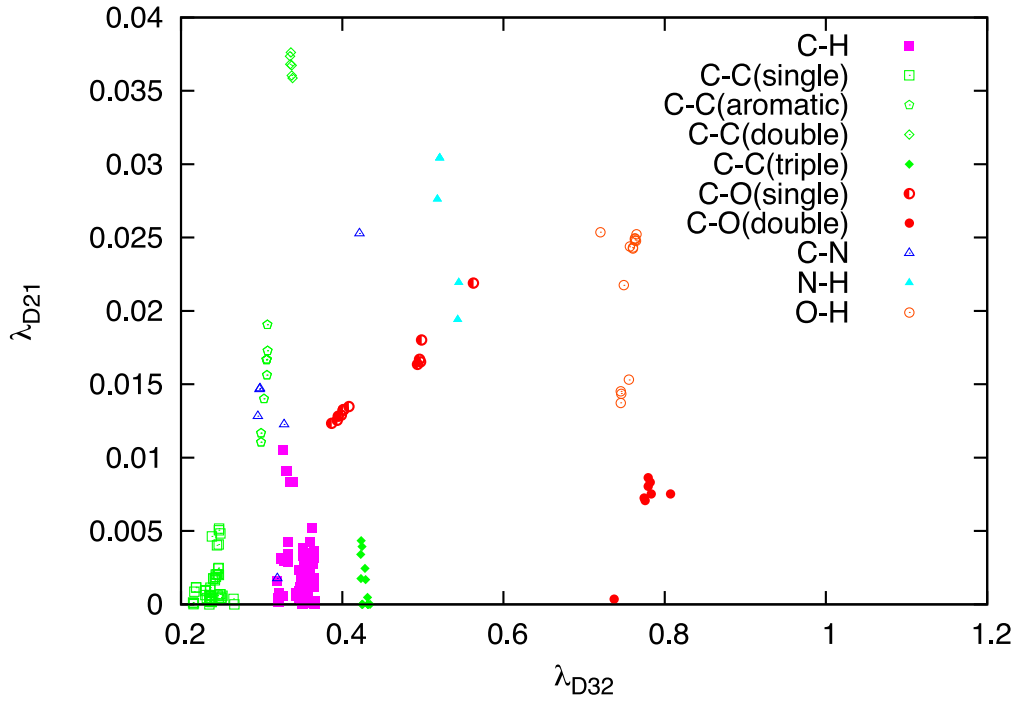


Fig. 9: The relation between the differential eigenvalues, $\lambda_{D32} = \lambda_3 - \lambda_2$ and $\lambda_{D21} = \lambda_2 - \lambda_1$, at the Lagrange points in the Li clusters (panel (a)) and hydrocarbon molecules (panel (b)). Note that the H_2 molecule has $\lambda_{D32} = 0.394$ and $\lambda_{D21} = 0$.

Supplementary Data

Contents

Fig. S1 Structures and bond order b_ϵ of hydrocarbon molecules.

Fig. S2 The relation between the bond length and three eigenvalues ($\lambda_3 \geq \lambda_2 \geq \lambda_1$) of the stress tensor at the Lagrange points of the C-C triple bonds in the hydrocarbon molecules.

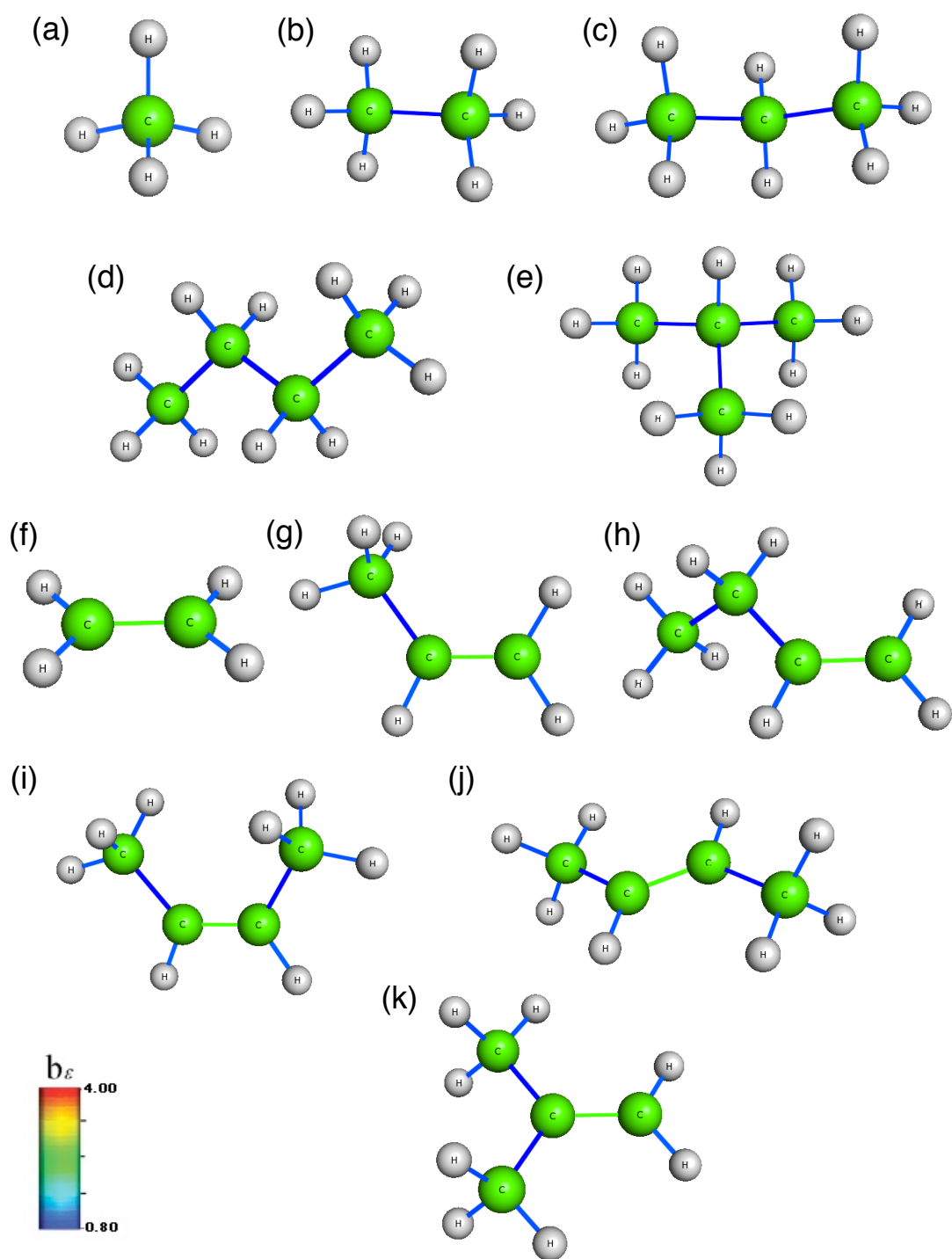


Fig. S10: Optimized structures of hydrocarbon molecules we use for our analysis. (a) methane, (b) ethane, (c) propane, (d) butane, (e) isobutane, (f) ethene, (g) propene, (h) 1-butene, (i) *cis*-2-butene, (j) *trans*-2-butene and (k) isobutene.

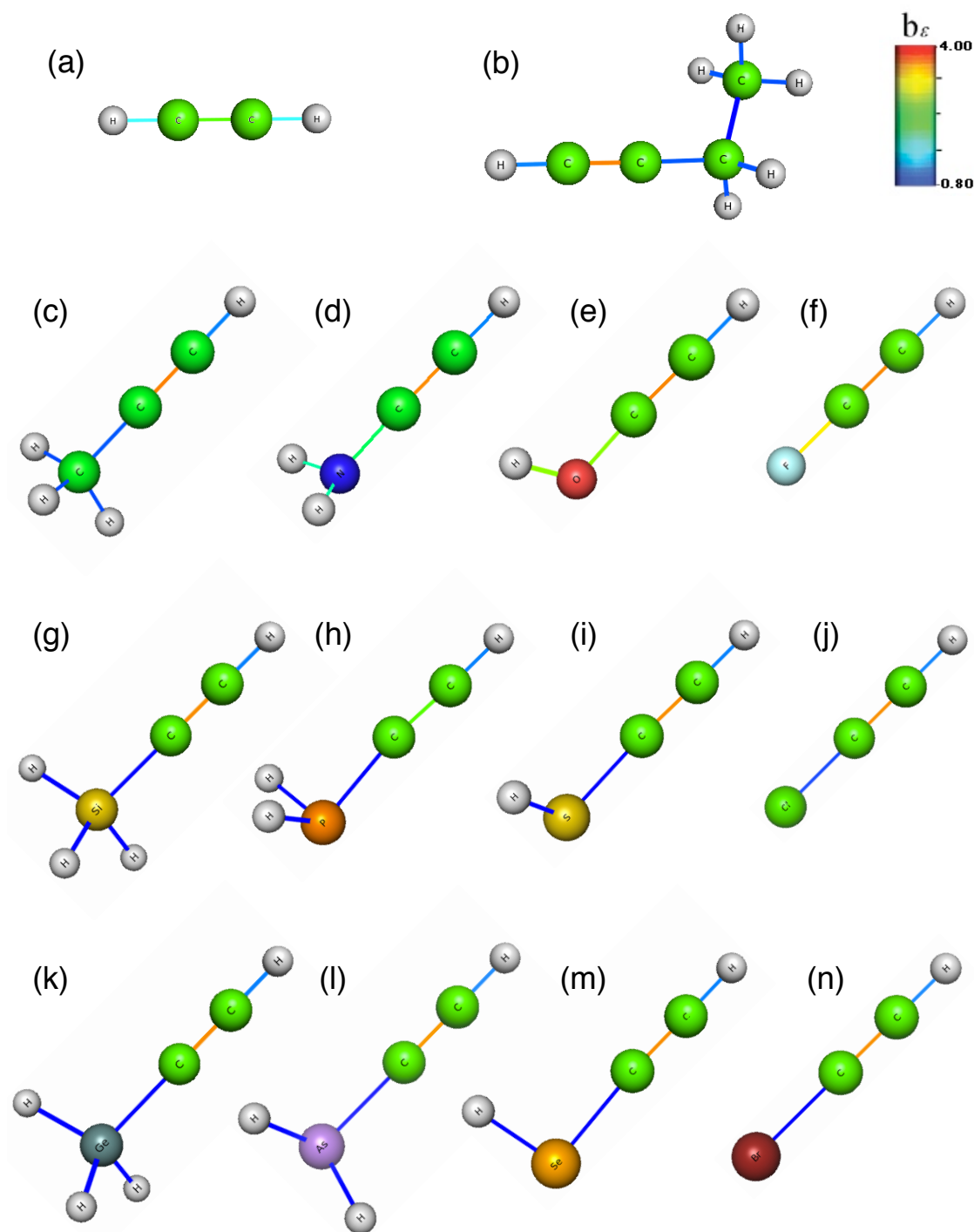


Fig. S1: (*continued*) Optimized structures of hydrocarbon molecules we use for our analysis. (a) ethyne and (b) butyne. (c)-(n) are C_2HX with X being (c) CH_3 (propyne), (d) NH_2 , (e) OH , (f) F , (g) SiH_3 , (h) PH_2 , (i) SH , (j) Cl , (k) GeH_3 , (l) AsH_2 , (m) SeH , (n) Br .

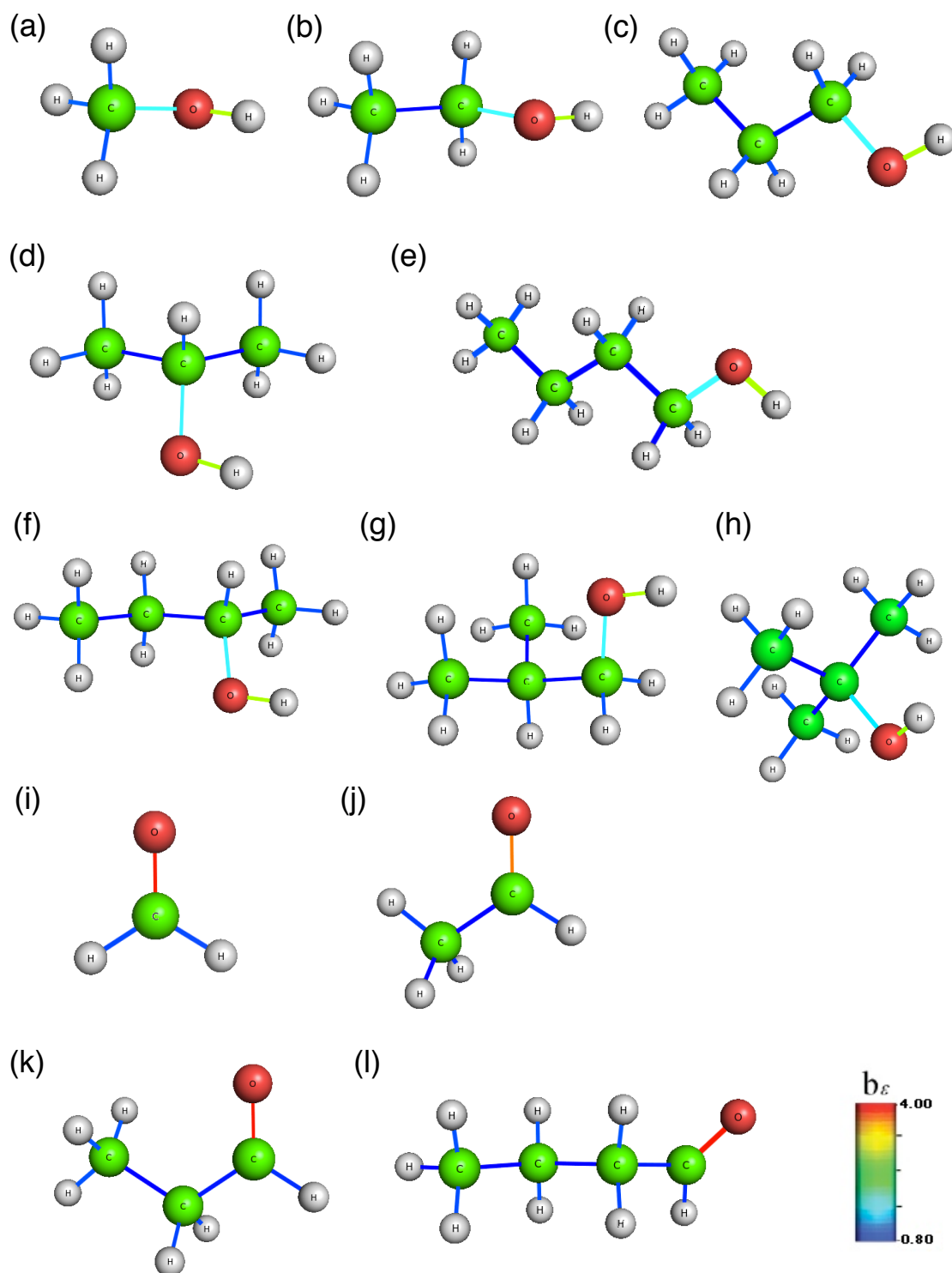


Fig. S1: (*continued*) Optimized structures of hydrocarbon molecules we use for our analysis. (a) methanol, (b) ethanol, (c) *n*-propanol, (d) isopropanol, (e) *n*-butanol, (f) *sec*-butanol, (g) isobutanol, (h) *tert*-butanol, (i) formaldehyde, (j) acetaldehyde, (k) propionaldehyde and (l) butyraldehyde.

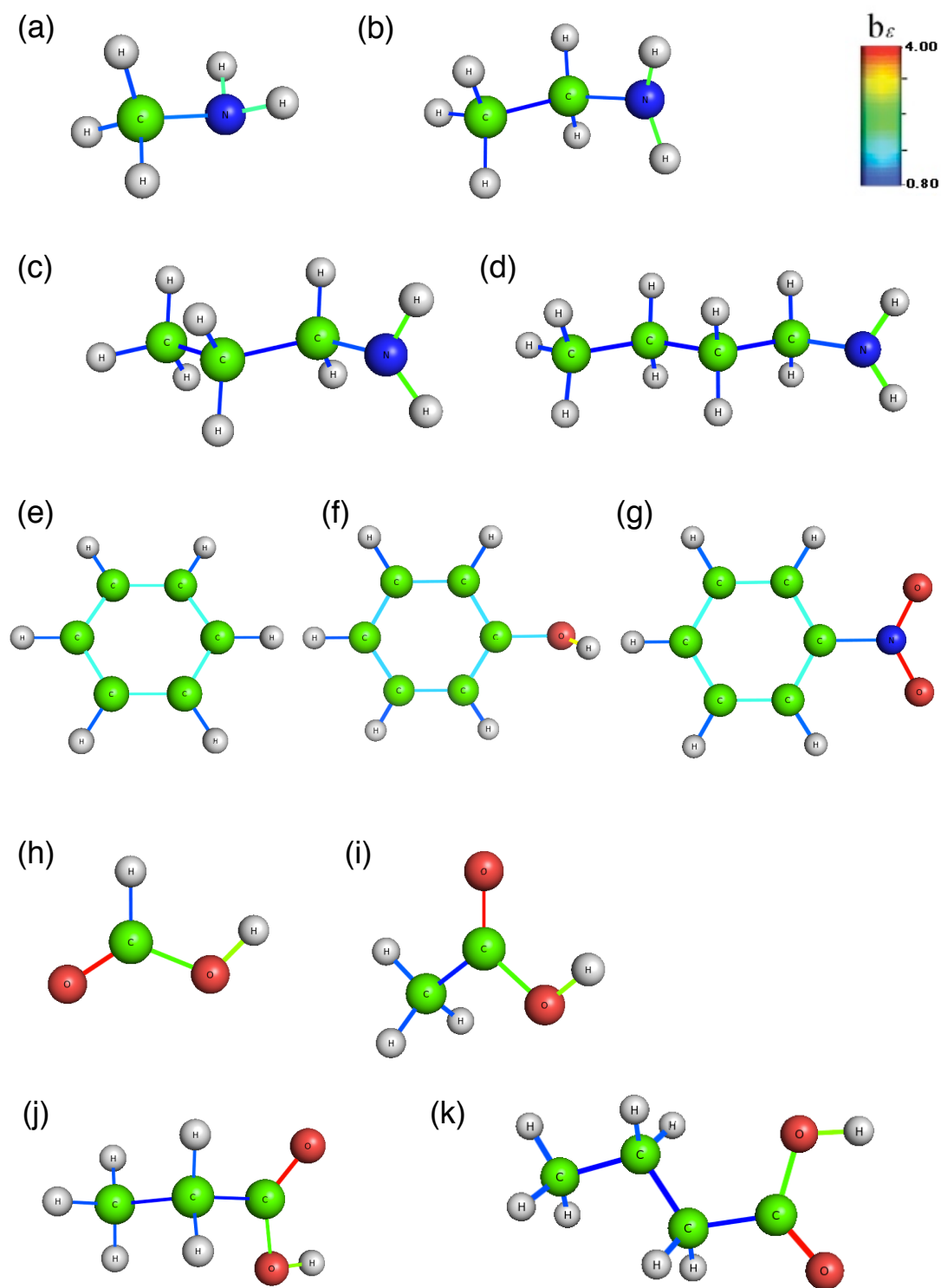


Fig. S1: (*continued*) Optimized structures of hydrocarbon molecules we use for our analysis. (a) methanamine, (b) ethanamine, (c) *n*-propanamine, (d) *n*-butanamine, (e) benzene, (f) phenol, (g) nitrobenzene, (h) formic acid, (i) acetic acid, (j) propionic acid and (k) butyric acid.

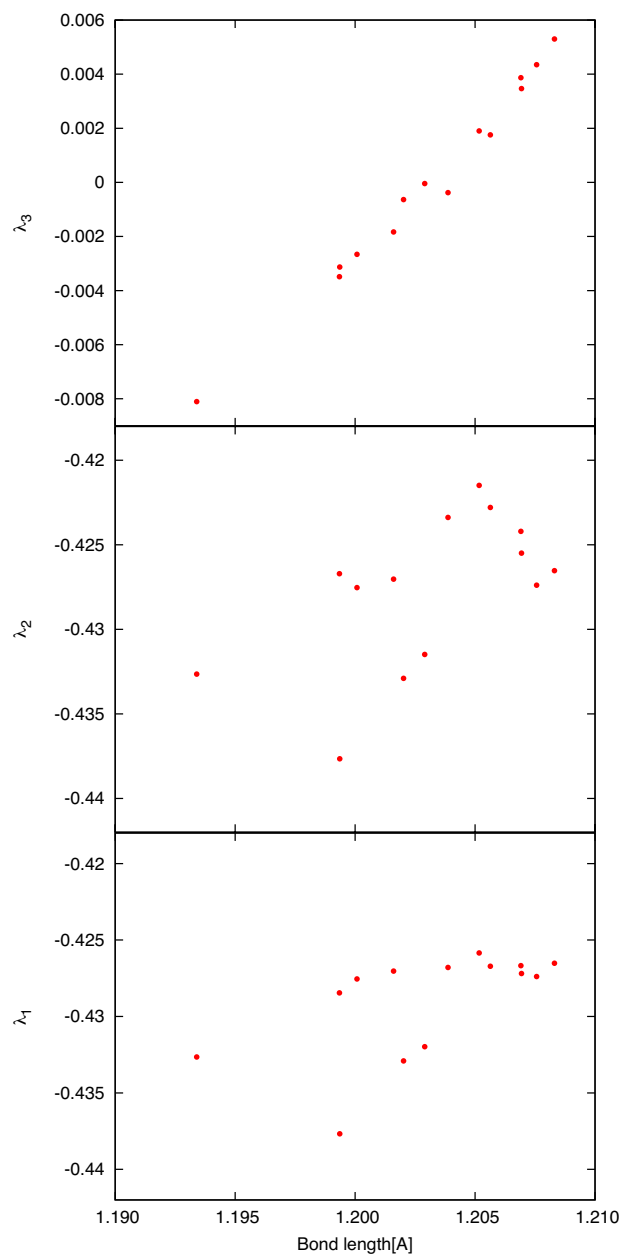


Fig. S2: The relation between the bond length and three eigenvalues ($\lambda_3 \geq \lambda_2 \geq \lambda_1$) of the stress tensor at the Lagrange points of the C-C triple bonds in the hydrocarbon molecules.

Chapter 3

3 Use of Electronic Stress Tensor Density and Energy Density in Chemistry

3.1 Introduction

The pioneering work of Heitler and London in 1927 succeeded in understanding the nature of chemical bonding based on quantum mechanics. Soon after the non-relativistic quantum mechanics was founded, physicists (including Heitler himself) developed quantum theory of electrodynamics which is now known as quantum electrodynamics (QED). QED is the theory of electronically charged particles and photons and interactions between them, taking the form of quantum theory of fields. After the theoretical developments and experimental verifications for several decades, it is considered as one of the most successful fundamental physical theory we have. Atomic and molecular systems, being the bound states of charged particles, are in principle described by QED. However, quantum chemistry has been almost always developed based the electrostatic Hamiltonian, and the effect of QED is only regarded as very small correction to the Coulomb potential. In order to understand the chemical bonding from the viewpoint of quantum field theory, one of the authors has developed the rigged QED (RQED) theory [8, 11]. In addition to the ordinary QED which is Lorentz invariant with Dirac field for electrons and $U(1)$ gauge field for photons, RQED is equipped (*i.e.* “rigged”) with Schrödinger fields which represent atomic nuclei. This enables us to describe atomic and molecular systems based on quantum field theory. In the next section, we introduce the physical quantity operators in RQED which are most relevant to our study of chemical bonding, and show relations among them. We also explain how we use them to derive the quantities to investigate the nature of chemical bonding.

Theory and calculation method

The most basic quantity in this study is the electronic stress tensor density operator $\hat{\tau}_e^{\Pi kl}(x)$ which is defined as follows [7].

$$\hat{\tau}_e^{\Pi kl}(x) = \frac{i\hbar c}{2} \left[\hat{\bar{\psi}}(x) \gamma^l \hat{D}_{ek}(x) \hat{\psi}(x) - \left(\hat{D}_{ek}(x) \hat{\psi}(x) \right)^\dagger \gamma^0 \gamma^l \hat{\psi}(x) \right], \quad (19)$$

where $\hat{\psi}(x)$ is the 4-component Dirac field operator for electrons. In this paper, we denote the spacetime coordinate as $x = (ct, \vec{r})$. The Latin letter indices like k and l express space coordinates from 1 to 3, and repeated indices implies a summation over 1 to 3. Here, the gauge covariant derivative is defined by

$$\hat{D}_{ek}(x) = \partial_k + i \frac{Z_e e}{\hbar c} \hat{A}_k(x), \quad Z_e = -1, \quad (20)$$

where $\hat{A}_k(x)$ is the vector potential of the photon field operator in the Coulomb gauge ($\text{div} \hat{\vec{A}}(x) = 0$). The important property of this quantity is that the time derivative of the electronic kinetic momentum density operator $\hat{\Pi}_e(x)$

$$\hat{\Pi}_e(x) = \frac{1}{2} \left(i\hbar \hat{\bar{\psi}}^\dagger(x) \hat{\vec{D}}_e(x) \hat{\psi}(x) - i\hbar \left(\hat{\vec{D}}_e(x) \hat{\psi}(x) \right)^\dagger \cdot \hat{\psi}(x) \right), \quad (21)$$

can be expressed by the sum of the Lorentz force density operator $\hat{\vec{L}}_e(x)$ and the tension density operator $\hat{\vec{\tau}}_e^{\Pi}(x)$, which is the divergence of the stress tensor density operator:

$$\frac{\partial}{\partial t} \hat{\Pi}_e(x) = \hat{\vec{L}}_e(x) + \hat{\vec{\tau}}_e^{\Pi}(x). \quad (22)$$

These operators are expressed as follows,

$$\hat{\vec{L}}_e(x) = \hat{\vec{E}}(x)\hat{\rho}_e(x) + \frac{1}{c}\hat{\vec{j}}_e(x) \times \hat{\vec{B}}(x), \quad (23)$$

$$\hat{\tau}_e^{\Pi k}(x) = \partial_l \hat{\tau}_e^{\Pi kl}(x) \quad (24)$$

$$\begin{aligned} &= \frac{i\hbar c}{2} \left[\left(\hat{D}_{el}(x)\hat{\psi}(x) \right)^\dagger \gamma^0 \gamma^l \cdot \hat{D}_{ek}(x)\hat{\psi}(x) + \hat{\psi}(x)\gamma^l \hat{D}_{ek}(x)\hat{D}_{el}(x)\hat{\psi}(x) \right. \\ &\quad \left. - \left(\hat{D}_{ek}(x)\hat{D}_{el}(x)\hat{\psi}(x) \right)^\dagger \gamma^0 \gamma^l \cdot \hat{\psi}(x) - \left(\hat{D}_{ek}(x)\hat{\psi}(x) \right)^\dagger \gamma^0 \gamma^l \cdot \hat{D}_{el}(x)\hat{\psi}(x) \right] \\ &\quad - \frac{1}{c} \left(\hat{\vec{j}}_e(x) \times \hat{\vec{B}}(x) \right)^k \end{aligned} \quad (25)$$

where $\hat{\vec{E}}(x)$ and $\hat{\vec{B}}(x)$ denote the electromagnetic field operators, and $\hat{\rho}_e(x)$ and $\hat{\vec{j}}_e(x)$ are electronic charge density operator and charge current density operator respectively. By taking the expectation values of Eq. (34) with respect to some stationary state, we obtain the equilibrium equation as

$$0 = \langle \hat{\vec{L}}_e(x) \rangle + \langle \hat{\tau}_e^{\Pi}(x) \rangle = \langle \hat{\vec{L}}_e(x) \rangle + \partial_l \langle \hat{\tau}_e^{\Pi kl}(x) \rangle, \quad (26)$$

which shows the balance between electromagnetic force and quantum field force at each point in space. Since this expresses the fact that the latter force keeps the electrons in the stationary bound state in atomic and molecular systems, we can expect to study the nature of chemical bonding from the viewpoint of quantum field theory by using the stress tensor density and tension density. In practice, we apply the primary rigged QED approximation [12], in which the small components of the 4-component electron field are expressed by the large components as $\hat{\psi}_S(x) \approx -\frac{1}{2mc}i\hbar\sigma^k D_k \hat{\psi}_L(x)$ and the spin-dependent terms are ignored, and we take the expectation value with respect to the stationary state of the electrostatic Hamiltonian. These assumptions lead to the following definitions of the stress tensor density $\tau^{Sk}(\vec{r})$ and tension density $\tau^{Sk}(\vec{r})$ we use in this study.

$$\tau^{Sk}(\vec{r}) = \frac{\hbar^2}{4m} \sum_i \nu_i \left[\psi_i^*(\vec{r}) \frac{\partial^2 \psi_i(\vec{r})}{\partial x^k \partial x^l} - \frac{\partial \psi_i^*(\vec{r})}{\partial x^k} \frac{\partial \psi_i(\vec{r})}{\partial x^l} + \frac{\partial^2 \psi_i^*(\vec{r})}{\partial x^k \partial x^l} \psi_i(\vec{r}) - \frac{\partial \psi_i^*(\vec{r})}{\partial x^l} \frac{\partial \psi_i(\vec{r})}{\partial x^k} \right], \quad (27)$$

$$\begin{aligned} \tau^{Sk}(\vec{r}) &= \partial_l \tau^{Sk l}(\vec{r}) \\ &= \frac{\hbar^2}{4m} \sum_i \nu_i \left[\psi_i^*(\vec{r}) \frac{\partial \Delta \psi_i(\vec{r})}{\partial x^k} - \frac{\partial \psi_i^*(\vec{r})}{\partial x^k} \Delta \psi_i(\vec{r}) + \frac{\partial \Delta \psi_i^*(\vec{r})}{\partial x^k} \psi_i(\vec{r}) - \Delta \psi_i^*(\vec{r}) \frac{\partial \psi_i(\vec{r})}{\partial x^k} \right], \end{aligned} \quad (28)$$

where $\psi_i(\vec{r})$ is the i th natural orbital and ν_i is its occupation number. Since the stress tensor is an Hermitian matrix, its eigenvalues are real and eigenvectors are orthogonal to each other. We denote the eigenvalues by λ_i ($i = 1, 2, 3$) with the ordering of $\lambda_3 \geq \lambda_2 \geq \lambda_1$. The concept of ‘‘Lagrange point’’ is proposed in Ref. [32] and we use it as a point which can characterize a bond between two atoms. The Lagrange point $\vec{r}_L$ is the point where the tension density $\vec{\tau}^S(\vec{r})$ vanishes: $\tau^{Sk}(\vec{r}_L) = 0$. We report the eigenvalues of electronic stress tensor at this point in the following sections.

We can define the energy density $\varepsilon_\tau^S(\vec{r})$ using the stress tensor. Ref. [7], proposes to use a half of the trace of the stress tensor $\varepsilon_\tau^S(\vec{r}) = \frac{1}{2} \sum_{k=1}^3 \tau^{Skk}(\vec{r})$ as the energy density. It can be defined as the energy density in a sense that the integration over whole space gives usual total energy E of the system: $\int \varepsilon_\tau^S(\vec{r}) d\vec{r} = E$, by using the virial theorem.

Another important quantity is the electronic kinetic energy density $n_T(\vec{r})$. By applying the above procedure which is used to define the stress tensor to the electronic kinetic energy density operator defined as follows [7],

$$\hat{T}_e(x) = -\frac{\hbar^2}{2m} \cdot \frac{1}{2} \left(\hat{\psi}^\dagger(x) \hat{D}_e^2(x) \hat{\psi}(x) + \left(\hat{D}_e^2(x) \hat{\psi}(x) \right)^\dagger \cdot \hat{\psi}(x) \right), \quad (29)$$

we obtain the definition for the electronic kinetic energy density as

$$n_T(\vec{r}) = -\frac{\hbar^2}{4m} \sum_i \nu_i [\psi_i^*(\vec{r}) \Delta \psi_i(\vec{r}) + \Delta \psi_i^*(\vec{r}) \cdot \psi_i(\vec{r})]. \quad (30)$$

Note that our definition of the kinetic energy density is not positive-definite. Using this kinetic energy density, we can divide the whole space into three types of region: the electronic drop region R_D with $n_T(\vec{r}) > 0$, where classically allowed motion of electron is guaranteed and the electron density is amply accumulated; the electronic atmosphere region R_A with $n_T(\vec{r}) < 0$, where the motion of electron is classically forbidden and the electron density is dried up; and the electronic interface S with $n_T(\vec{r}) = 0$, the boundary between R_D and R_A , which corresponds to a turning point. The S can give a clear image of the intrinsic shape of atoms and molecules and is therefore an important region in particular.

The electronic structures used in this paper are obtained by the Gaussian 09 [58]. To compute the stress tensor density (Eq. (39)), tension density (Eq. (40)) and kinetic energy density (Eq. (30)), from the electronic structure data, we use the QEDynamics package [34].

3.2 Results and discussion

Electronic interface and size of atoms We compute the electronic interface, S , for atoms of elements in the first, second and third periods. Spin multiplicities are chosen to give their ground states. As for the electron configuration regarding the p orbitals, we choose them to be occupied in the alphabetical order p_x, p_y, p_z . Our findings can be summarized as follows. At first, we find that the shapes of S have the symmetry which is expected from the orbital angular momentum and electron configurations of each atom. Then, we propose that S_{outer} , the outermost S , can be regarded as the intrinsic shape of the atoms. We point out that, in most cases, the region inside S_{outer} is divided into two R_D 's by the nearly spherical-shell-shaped R_A . For these two R_D 's, we associate the inner R_D as the core shell and the outer R_D as the valence shell. This interpretation is supported by the integrated electron number in the core region, and also by the size of S_{outer} of the cations which are constructed by removing all the electrons in the outermost shell. We denote the boundary surface of core shell as S_{inner} , and investigate the size of S_{outer} and S_{inner} . Then, as shown in Fig. 1, left panel, we see the clear periodicity for the size of S_{outer} and S_{inner} with respect to the nuclear charge. In the figure, we compare the size of S_{outer} and S_{inner} respectively with the atomic and ionic radii in the literature [8,9]. We would like to emphasize that the shape and size of atoms studied here are defined for the isolated atoms and intrinsic to them. Such a definition is more advantageous than the conventional atomic and ionic radii which are determined from internuclear distances in compounds and crystals, when we study intrinsic aspects of atoms.

3.3 Lagrange surface

The tension density, Eq. (40), defines vector field for atoms and molecules. The tension vector field exhibits a pattern such that the vectors originate from the atomic nuclei and radiate in all directions. This reflects the repulsive electronic tension which compensates the attractive electric field of atomic nucleus. In other words, the repulsive electronic tension drives the quantum mechanical electronic diffusion, which keeps the electrons to be bounded. In a molecule, the tension vectors originate from atomic centers collide to form separatrixes, and they discriminates regions which belongs to each atomic nucleus. Thus, we can use vector field of the tension density to define boundary surfaces of atoms in a molecule as separatrix of the field [12]. We designate this surface as ‘‘Lagrange surface’’ [11]. The case for a HF molecule is depicted in the right panel of Fig. 1.

Energy density based bond order and spring constant In Ref. [32], it is proposed that new bond orders (bond strength indices) can be defined by using the energy density $\varepsilon_\tau^S(\vec{r})$ at a Lagrange point between two atoms. Our definition of bond order of a bond between nuclei A and B are $b_\varepsilon =$

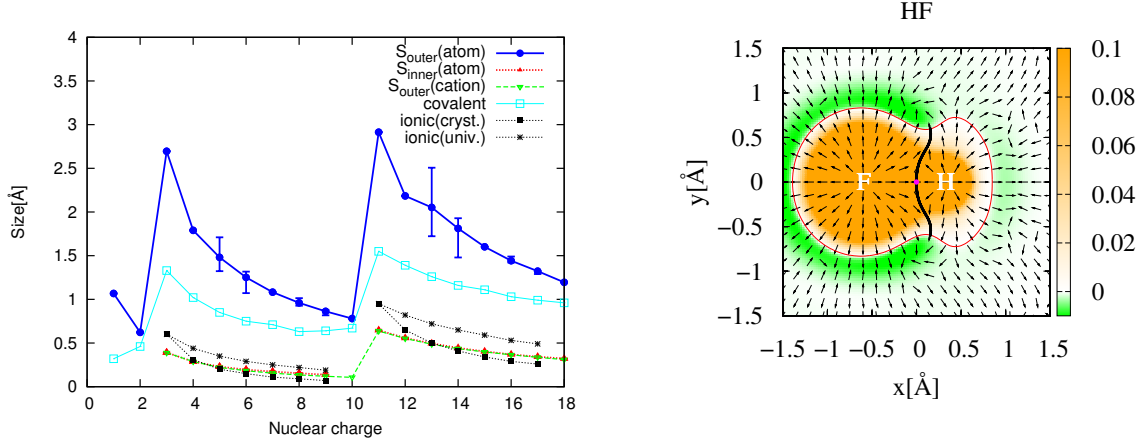


Fig. 1: In the left panel, the size of S_{outer} and S_{inner} of atoms, and S_{outer} of cations, are plotted. Covalent radii from Ref. [8] and ionic radii (the crystal radii and univalent radii) from Ref. [9] are also plotted. In the right panel, tension vector field of HF molecule is plotted. The filled circle is the Lagrange point and the thick solid line is the Lagrange surface. Thin solid line denotes the electronic interface of the HF molecule.

$\varepsilon_{\tau AB}^S(\vec{r}_L)/\varepsilon_{\tau HH}^S(\vec{r}_L)$, where the expression like $\varepsilon_{\tau AB}^S(\vec{r}_L)$ means the energy density evaluated at the Lagrange point found between A and B. One should note we normalize by the value of a H₂ molecule calculated at the same level of theory (including method and basis set). So far, we have investigated a correlation between this new bond order b_ε and bond distance in *e.g.* Refs. [34, 40], and have found that b_ε exhibits better correlation than other bond orders proposed in the literature. However, we have not investigated a correlation between b_ε and a quantity related to energy. We have found that a correlation with the bond dissociation energy is very poor. We then investigate a correlation with “spring constant” k_{AB} , which is calculated based on the directional derivative of a total energy E of a molecule regarding the bond direction. This is defined as

$$k_{AB} = -\frac{\partial^2 E}{\partial \vec{s}_{AB} \partial \vec{s}_{AB}} = -(\cos \alpha, \cos \beta, \cos \gamma) \begin{pmatrix} \frac{\partial^2 E}{\partial x_A \partial x_B} & \frac{\partial^2 E}{\partial x_A \partial y_B} & \frac{\partial^2 E}{\partial x_A \partial z_B} \\ \frac{\partial^2 E}{\partial y_A \partial x_B} & \frac{\partial^2 E}{\partial y_A \partial y_B} & \frac{\partial^2 E}{\partial y_A \partial z_B} \\ \frac{\partial^2 E}{\partial z_A \partial x_B} & \frac{\partial^2 E}{\partial z_A \partial y_B} & \frac{\partial^2 E}{\partial z_A \partial z_B} \end{pmatrix} \begin{pmatrix} \cos \alpha \\ \cos \beta \\ \cos \gamma \end{pmatrix}, \quad (31)$$

where $\vec{s}_{AB} = (\cos \alpha, \cos \beta, \cos \gamma)$ is the direction of the bond. As shown in Eq. (31), k_{AB} can be obtained by using a part of a force constant matrix of the molecule. We compute b_ε and k_{AB} for the molecules which may exist in gas phase of chemical vapor deposition (CVD) process for Ge₂Sb₂Te₅, the most popular material for phase change memory (PCM). The result is shown in the left panel of Fig. 2, and we see a very good correlation between these two quantities.

Electronic stress tensor analysis and covalent/metallic bond In recent paper, Ref. [42], we have pointed out that we may characterize a metallic nature of chemical bonding in terms of the electronic stress tensor. We have analyzed the bonding region in small cluster models and periodic models of Li and Na using the electronic stress tensor, and have found that all the three eigenvalues are negative and degenerate, just like the stress tensor of liquid. This is in stark contrast to hydrocarbon molecules, which have the positive largest eigenvalue much larger than the other two negative eigenvalues. The eigenvalue pattern of Li and Na indicates lack of directionality and compressive nature of bonding, while that of hydrocarbon molecules indicates solid directionality and tensile nature of bonding. As argued in Ref. [42] (the case of covalent bonding has been discussed originally in Ref. [9]), each pattern well reflects the nature of metallic and covalent bonding. Note that the negativity and degeneracy of the

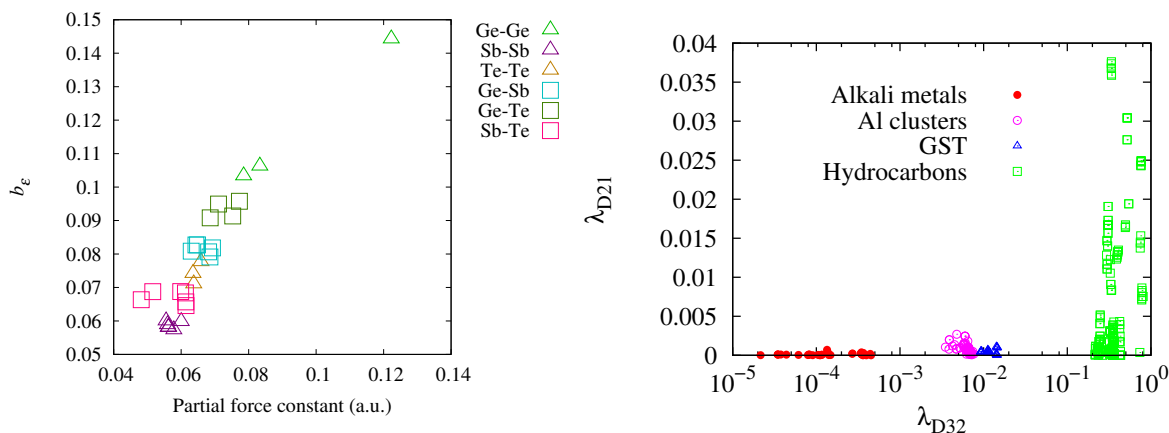


Fig. 2: In the left panel, a correlation between the energy density based bond order b_ϵ and the spring constant k_{AB} is plotted. In the right panel, the differential eigenvalues are plotted.

stress tensor, which is the property of the liquid, is readily associated with the conventional description that the metallic bonding can be viewed as “electron sea”. This degeneracy of the eigenvalues of the electronic stress tensor is shown in the right panel of Fig. 2, in terms of the differential eigenvalues, $\lambda_{D32} \equiv \lambda_3 - \lambda_2$ and $\lambda_{D21} \equiv \lambda_2 - \lambda_1$. In the figure, in addition to the hydrocarbon molecules and alkali metal clusters, we show the results for bonds between semimetal atoms. From the viewpoint of the stress tensor eigenvalues, the bonds between these semimetal atoms are found to have intermediate nature between covalent and metallic bonds.

3.4 Summary

We have introduced the electronic stress tensor density, energy density, tension density and kinetic energy density, which are quantities based on quantum field theory, and discussed their use in chemistry for four aspects: (i) electronic interface (zero surface of the electronic kinetic energy density) and size of atoms, (ii) Lagrange surface (separatrix of the tension field) as a boundary surface of atoms in a molecule, (iii) interpretation of energy density based bond order as spring constant (directional derivative of a total energy of a molecule regarding the bond direction), and (iv) eigenvalues of the electronic stress tensor to classify the bond type. The topics discussed here are only limited examples of the field theoretic approach for chemistry. Further applications will deepen our understanding of the nature of chemical bonding.

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Chapter 4

4 Electronic Stress Tensor Analysis of Molecules in Gas Phase of CVD Process for GeSbTe Alloy

4.1 Introduction

GeSbTe (GST) alloy is the most popular material for phase change memory (PCM) [1, 2], which is one of the most promising candidates for the next-generation memory device. So far, GST thin films are deposited by physical vapor deposition such as sputtering and pulsed laser deposition. However, chemical vapor deposition (CVD) of GST [3–5] has many advantages such as good step coverage, uniformity and high purity, and considered to be necessary for future PCM applications. The CVD process for GST is relatively a new field of research and there remains many things which are not clearly known. One of them is the chemical reactions in the gas phase of CVD process, and we have investigated reactions and molecules which may exist in the gas phase using quantum chemical calculation [6]. As the result of this study, we have obtained a data set of molecules which have bonds among Ge, Sb and Te. In this paper, we apply our electronic stress tensor analysis based on the Rigged QED (Quantum Electrodynamics) theory [7–13] to this data set, and investigate how these bonds can be described by the electronic stress tensor.

In general, the stress tensor, which describes a pattern of internal forces of matter, is widely used in various fields of science such as mechanical engineering and material science. The use of stress tensor in quantum systems as well has been investigated for many years, by one of the earliest quantum mechanics papers [14, 15] and many researchers [16–31] including our group [7–13, 32–42]. In our past studies, we have shown that the electronic stress tensor and related quantities can be useful tools to analyze atomic and molecular systems and can give new viewpoints on the nature of chemical bonding.

We here introduce two of our findings which we wish to investigate more deeply using GST bonds in this paper. First, we have pointed out that we may characterize some aspects of a metallic bond or metallicity of a chemical bond in terms of the electronic stress tensor [32, 42]. We have analyzed the bonding region in the small cluster models and periodic models of Li and Na using the electronic stress tensor, and have found that all the three eigenvalues of the stress tensor are negative and degenerate, just like those of liquid. This is in stark contrast to hydrocarbon molecules, which have the positive largest eigenvalue much larger than the other two negative eigenvalues. The eigenvalue pattern of Li and Na indicates a lack of directionality and compressive nature of bonding while that of hydrocarbon molecules indicates solid directionality and tensile nature of bonding. Each pattern well reflects the nature of metallic and covalent bonding. Then, the question worth asking is, how the chemical bonds between metalloid atoms like Ge, Sb and Te are described by the electronic stress tensor. Second, using the energy density which is defined from the electronic stress tensor, new definition of bond order has been proposed [32]. So far, we have investigated a correlation between this new bond order and bond distance [32–34, 40], and have found that our bond order exhibits better correlation than the other bond orders proposed in the literature. We, however, have not investigated a correlation with a quantity related to energy. Therefore, we wish to investigate a correlation between our bond order and the bond dissociation energy, which is available in our data set as the dimerization energy of the CVD precursors. In addition, we compute a force constant for the GST bonds and examine a correlation with our bond order.

The structure of this paper is as follows. Sec. 4.2 summarizes our analysis method of electronic structures using the electronic stress tensor density. In Sec. 4.3, we show the electronic stress tensor density and its eigenvalues of the GST bonds, and compare with those of hydrocarbon molecules and alkali metal clusters. We also investigate correlations between our bond order and energy-related quantities. Finally, Sec. 4.4 is devoted to our conclusion.

4.2 Theory

In the following subsection, we analyze chemical bonds using quantities such as the electronic stress tensor density and the kinetic energy density. They are based on the Rigged QED theory [8] and we briefly describe them in this subsection. The Rigged QED is a quantum field theory which has been proposed [8] to treat dynamics of charged particles and photons in atomic and molecular systems. In addition to the ordinary QED which contains the Dirac field for electrons and the gauge field for photons, the Schrödinger fields for atomic nuclei are included. More details are found in our previous papers [7, 8, 11–13]. Below, c denotes the speed of light in vacuum, $\hbar$ the reduced Planck constant, e the electron charge magnitude (so that e is positive), and m the electron mass. The gamma matrices are denoted by γ^μ ($\mu=0-3$).

The most basic quantity in the Rigged QED is the electronic stress tensor density operator $\hat{\tau}_e^{\Pi kl}(x)$ which is defined as follows [7].

$$\hat{\tau}_e^{\Pi kl}(x) = \frac{i\hbar c}{2} \left[\hat{\psi}(x) \gamma^l \hat{D}_{ek}(x) \hat{\psi}(x) - \left(\hat{D}_{ek}(x) \hat{\psi}(x) \right)^\dagger \gamma^0 \gamma^l \hat{\psi}(x) \right], \quad (32)$$

where $\hat{\psi}(x)$ is the four-component Dirac field operator for electrons, the dagger as a superscript is used to express Hermite conjugate, and $\hat{\bar{\psi}}(x) \equiv \hat{\psi}^\dagger(x) \gamma^0$. We denote the spacetime coordinate as $x = (ct, \vec{r})$. The Latin letter indices like k and l express space coordinates from 1 to 3. Here, the gauge covariant derivative is defined by $\hat{D}_{ek}(x) = \partial_k + i \frac{Z_e e}{\hbar c} \hat{A}_k(x)$, where $Z_e = -1$, and $\hat{A}_k(x)$ is the vector potential of the photon field operator in the Coulomb gauge ($\text{div} \hat{A}(x) = 0$). The important property of this quantity is that the time derivative of the electronic kinetic momentum density operator $\hat{\Pi}_e(x)$

$$\hat{\Pi}_e(x) = \frac{1}{2} \left(i\hbar \hat{\psi}^\dagger(x) \hat{D}_e(x) \hat{\psi}(x) - i\hbar \left(\hat{D}_e(x) \hat{\psi}(x) \right)^\dagger \cdot \hat{\psi}(x) \right), \quad (33)$$

can be expressed by the sum of the Lorentz force density operator $\hat{L}_e(x)$ and the tension density operator $\hat{\tau}_e^{\Pi}(x)$, which is the divergence of the stress tensor density operator:

$$\frac{\partial}{\partial t} \hat{\Pi}_e(x) = \hat{L}_e(x) + \hat{\tau}_e^{\Pi}(x). \quad (34)$$

These operators are expressed as follows,

$$\hat{L}_e(x) = \hat{E}(x) \hat{\rho}_e(x) + \frac{1}{c} \hat{\vec{j}}_e(x) \times \hat{B}(x), \quad (35)$$

$$\hat{\tau}_e^{\Pi k}(x) = \partial_l \hat{\tau}_e^{\Pi kl}(x) \quad (36)$$

$$\begin{aligned} &= \frac{i\hbar c}{2} \left[\left(\hat{D}_{el}(x) \hat{\psi}(x) \right)^\dagger \gamma^0 \gamma^l \cdot \hat{D}_{ek}(x) \hat{\psi}(x) + \hat{\bar{\psi}}(x) \gamma^l \hat{D}_{ek}(x) \hat{D}_{el}(x) \hat{\psi}(x) \right. \\ &\quad \left. - \left(\hat{D}_{ek}(x) \hat{D}_{el}(x) \hat{\psi}(x) \right)^\dagger \gamma^0 \gamma^l \cdot \hat{\psi}(x) - \left(\hat{D}_{ek}(x) \hat{\psi}(x) \right)^\dagger \gamma^0 \gamma^l \cdot \hat{D}_{el}(x) \hat{\psi}(x) \right] \\ &\quad - \frac{1}{c} \left(\hat{\vec{j}}_e(x) \times \hat{B}(x) \right)^k, \end{aligned} \quad (37)$$

where $\hat{E}(x)$ and $\hat{B}(x)$ denote the electric field operator and magnetic field operator respectively, and $\hat{\rho}_e(x)$ and $\hat{\vec{j}}_e(x)$ are the electronic charge density operator and charge current density operator respectively.

For nonrelativistic systems, we approximate the expressions above in the framework of the Primary Rigged QED approximation [12, 13], in which the small components of the four-component electron field

are expressed by the large components as $\hat{\psi}_S(x) \approx -\frac{1}{2mc}i\hbar\sigma^k D_k \hat{\psi}_L(x)$ and the spin-dependent terms are ignored. Then, we take the expectation value of Eq. (34) with respect to the stationary state of the electrostatic Hamiltonian. This leads to the equilibrium equation as

$$0 = \langle \hat{L}_e(x) \rangle + \langle \hat{\tau}_e^S(x) \rangle = \langle \hat{L}_e(x) \rangle + \partial_l \langle \hat{\tau}_e^{Sk}(x) \rangle, \quad (38)$$

which shows the balance between electromagnetic force and quantum field force at each point in space. Since this expresses the fact that the latter force keeps the electrons in the stationary bound state in atomic and molecular systems, we can expect to study the nature of chemical bonding from the viewpoint of quantum field theory by using the stress tensor density and tension density. We express $\langle \hat{\tau}_e^S(x) \rangle$ and $\langle \hat{\tau}_e^{Sk}(x) \rangle$ respectively $\tau^{Sk}(\vec{r})$ and $\tau^{Sk}(\vec{r})$ for simplicity (we also write only spatial coordinate $\vec{r}$ because we consider stationary state). The explicit expression for the stress tensor density $\tau^{Sk}(\vec{r})$ and tension density $\tau^{Sk}(\vec{r})$ are

$$\begin{aligned} \tau_e^{Sk}(\vec{r}) = & \frac{\hbar^2}{4m} \sum_i \nu_i \left[\psi_i^*(\vec{r}) \frac{\partial^2 \psi_i(\vec{r})}{\partial x^k \partial x^l} - \frac{\partial \psi_i^*(\vec{r})}{\partial x^k} \frac{\partial \psi_i(\vec{r})}{\partial x^l} \right. \\ & \left. + \frac{\partial^2 \psi_i^*(\vec{r})}{\partial x^k \partial x^l} \psi_i(\vec{r}) - \frac{\partial \psi_i^*(\vec{r})}{\partial x^l} \frac{\partial \psi_i(\vec{r})}{\partial x^k} \right], \end{aligned} \quad (39)$$

$$\begin{aligned} \tau_e^{Sk}(\vec{r}) = & \sum_l \partial_l \tau^{Sk}(\vec{r}) \\ = & \frac{\hbar^2}{4m} \sum_i \nu_i \left[\psi_i^*(\vec{r}) \frac{\partial \Delta \psi_i(\vec{r})}{\partial x^k} - \frac{\partial \psi_i^*(\vec{r})}{\partial x^k} \Delta \psi_i(\vec{r}) \right. \\ & \left. + \frac{\partial \Delta \psi_i^*(\vec{r})}{\partial x^k} \psi_i(\vec{r}) - \Delta \psi_i^*(\vec{r}) \frac{\partial \psi_i(\vec{r})}{\partial x^k} \right], \end{aligned} \quad (40)$$

where $\psi_i(\vec{r})$ is the i th natural orbital and ν_i is its occupation number. Δ denotes the Laplacian, $\Delta \equiv \sum_{k=1}^3 (\partial/\partial x^k)^2$. When the density functional theory (DFT) method is used to compute the electronic structure, we use the Kohn-Sham orbitals for $\psi_i(\vec{r})$ in the above expressions. The eigenvalue of the symmetric tensor $\overset{\leftrightarrow}{\tau}^S$ is the principal stress and the eigenvector is the principal axis as follows:

$$\overset{\leftrightarrow}{\tau}_e^S(\vec{r}) = \begin{pmatrix} \tau_{e xx}^S(\vec{r}) & \tau_{e xy}^S(\vec{r}) & \tau_{e xz}^S(\vec{r}) \\ \tau_{e yx}^S(\vec{r}) & \tau_{e yy}^S(\vec{r}) & \tau_{e yz}^S(\vec{r}) \\ \tau_{e zx}^S(\vec{r}) & \tau_{e zy}^S(\vec{r}) & \tau_{e zz}^S(\vec{r}) \end{pmatrix} \quad (41)$$

$$\xrightarrow{\text{diag}} \begin{pmatrix} \tau_e^{S11}(\vec{r}) & 0 & 0 \\ 0 & \tau_e^{S22}(\vec{r}) & 0 \\ 0 & 0 & \tau_e^{S33}(\vec{r}) \end{pmatrix}, \tau_e^{S11}(\vec{r}) \leq \tau_e^{S22}(\vec{r}) \leq \tau_e^{S33}(\vec{r}). \quad (42)$$

We use a concept of ‘‘Lagrange point’’ [32] to characterize a bond between two atoms. The Lagrange point $\vec{r}_L$ is defined as the point where the tension density $\vec{\tau}^S(\vec{r})$ vanishes, namely $\tau^{Sk}(\vec{r}_L) = 0$. We analyze chemical bonds by computing the eigenvalues of electronic stress tensor density at this point.

Another important quantity in the Rigged QED is the electronic kinetic energy density operator defined as [7],

$$\hat{T}_e(x) = -\frac{\hbar^2}{2m} \cdot \frac{1}{2} \left(\hat{\psi}^\dagger(x) \hat{D}_e^2(x) \hat{\psi}(x) + \left(\hat{D}_e^2(x) \hat{\psi}(x) \right)^\dagger \cdot \hat{\psi}(x) \right). \quad (43)$$

As is done for the electronic stress tensor density operator, we apply the Primary Rigged QED approximation to Eq. (43) and take the expectation value with respect to the stationary state of the

electrostatic Hamiltonian. Then, we obtain the definition for the electronic kinetic energy density as

$$n_{T_e}(\vec{r}) = -\frac{\hbar^2}{4m} \sum_i \nu_i [\psi_i^*(\vec{r}) \Delta \psi_i(\vec{r}) + \Delta \psi_i^*(\vec{r}) \cdot \psi_i(\vec{r})]. \quad (44)$$

Note that our definition of the electronic kinetic energy density is not positive-definite. Using this kinetic energy density, we can divide the whole space into three types of region: the electronic drop region R_D with $n_{T_e}(\vec{r}) > 0$, where classically allowed motion of electron is guaranteed and the electron density is amply accumulated; the electronic atmosphere region R_A with $n_{T_e}(\vec{r}) < 0$, where the motion of electron is classically forbidden and the electron density is dried up; and the electronic interface S with $n_{T_e}(\vec{r}) = 0$, the boundary between R_D and R_A , which corresponds to a turning point. The S can give a clear image of the intrinsic shape of atoms and molecules and is, therefore, an important region in particular.

Finally, in our analysis, we use the energy density $\varepsilon_\tau^S(\vec{r})$ which is defined as a half of the trace of the stress tensor density [7]:

$$\varepsilon_\tau^S(\vec{r}) = \frac{1}{2} \sum_{k=1}^3 \tau^{Skk}(\vec{r}). \quad (45)$$

It can be regarded as the energy density in a sense that the integration over whole space gives usual total energy E of the system: $\int \varepsilon_\tau^S(\vec{r}) d\vec{r} = E$. This can be proved by using the virial theorem. Using this energy density $\varepsilon_\tau^S(\vec{r})$, a new definition of the bond order (bond strength index) is proposed [32]. It is defined as $\varepsilon_\tau^S(\vec{r})$ at the Lagrange point between two atoms. Our definition of bond order between atoms A and B is

$$b_e = \frac{\varepsilon_{\tau AB}^S(\vec{r}_L)}{\varepsilon_{\tau HH}^S(\vec{r}_L)}. \quad (46)$$

One should note we normalize by the value of a H_2 molecule calculated at the same level of theory (including method and basis set).

4.3 Results and discussion

4.3.1 Data set and computational details

Our data set consists of 35 molecules (Table 1, the leftmost column) which may exist in the gas phase of CVD process for GeSbTe alloy. They could be formed by reactions among GST precursors and/or H_2 carrier gas, and each of them has a bond between Ge, Sb or Te atoms. Their geometries and coordinates are given in the supplementary material (Fig. S1). For the precursors, we assume *tert*-Butylgermanium ($GeH_3(tBu)$, Fig. 1(a)) for the Ge precursor, triisopropylantimony ($Sb(iPr)_3$, Fig. 1(b)) for the Sb precursor, and diisopropyltellurium ($Te(iPr)_2$, Fig. 1(c)) for the Te precursor [5]. They are optimized by the DFT method based on the Lee-Yang-Parr gradient-corrected functional [43, 44] with Becke's three hybrid parameters [45] (B3LYP). Threshold for maximum force is set to 0.000450 hartree/bohr. The Dunning-Huzinaga double-zeta basis set [46] with effective core potential by Hay and Wadt [47–49] (LanL2DZ) are used for Ge, Sb and Te atoms. 6-31G(d) [50, 51] basis set is used for C atoms. D95(d,p) [46] basis set is employed for H atoms. Total energies at 0 K is obtained including zero-point energies with a scaling factor for B3LYP, 0.980 [52].

We also use Ge, Sb and Te crystal structures [53–55] as a reference data. We use the norm-conserving pseudopotentials of Troullier-Martins type [56] and the generalized-gradient approximation method by Perdew-Burke-Ernzerhof [57] for density functional exchange-correlation interactions. Kinetic energy cutoff of plane-wave expansion (k-point) is taken as 40.0 hartree ($2 \times 2 \times 2$ k-point set).

The electronic structures used in this paper are obtained by Gaussian 09 [58] for cluster models and by ABINIT [59, 60] for periodic models. We use the QEDynamics package [34] developed in our group to compute the quantities described in the previous subsection such as Eqs. (39), (40) and (44).

4.3.2 Electronic stress tensor and its eigenvalues

We begin by briefly reviewing our past works on the electronic stress tensor analysis which are related to the present paper. First, it has been proposed that a covalent bond can be described by the eigenvalues and eigenvectors of the electronic stress tensor [9]. In detail, the bonding region with covalency can be characterized and visualized by the “spindle structure”, where the largest eigenvalue of the electronic stress tensor is positive and the corresponding eigenvectors form a bundle of flow lines that connects nuclei. As an example, we show a map of the largest eigenvalue of the electronic stress tensor including a region between C atoms of $\text{GeH}_3(\text{tBu})$ in Fig. 2 (a), where we can find the spindle structure. In passing, in Fig. 2 (b), we show the tension density and the Lagrange point for the same C-C bond. Then, we have proposed that the negativity of the three eigenvalues of the stress tensor and their degeneracy, which is the same pattern as liquid, can characterize some aspects of the metallic nature of chemical bonding [32,42]. In Ref. [42], it has been shown that the three eigenvalues of the Li and Na clusters have almost same values while the hydrocarbon molecules have the largest eigenvalue much larger than the second largest eigenvalue, which has similar value to the smallest eigenvalue. In terms of the differential eigenvalues, the Li and Na clusters have very small $\tau_e^{S33} - \tau_e^{S22}$ and $\tau_e^{S22} - \tau_e^{S11}$ which are much smaller than $\tau_e^{S33} - \tau_e^{S22}$ of hydrocarbons. The former degeneracy pattern indicates that the bonds are not directional while the latter indicates the clear directionality of the bonds, reflecting the metallic nature of chemical bonding in the alkali metal clusters and the covalent nature of bonding in the hydrocarbon molecules.

Now, let us move on to study the electronic stress tensor of the GST bonds. We first show a map of τ_e^{S33} and corresponding eigenvector on a plane which contains a bond between GST atoms in Fig.3. We find a Lagrange point between each bond and its position is marked in the figure. A common feature we see in all the six panels is that the eigenvectors form a pattern which connects GST nuclei. However, not all of them are spindle structures. As for the Ge-Ge (panel (a)) and Ge-Sb (panel (d)) bonds, since they do not exhibit a positive τ_e^{S33} region, they are called to have pseudo-spindle structures [40]. As for the Te-Te (panel (c)) and Sb-Te (panel (f)) bonds, although we may say they have spindle structures, the positive regions are not as conspicuous as the spindle structure of the C-C bond seen in Fig. 2 (a). As for the Sb-Sb (panel (b)) and Ge-Te (panel (e)) bonds, the positive τ_e^{S33} regions are even smaller. These results lead us to conclude that the GST atoms have the ability to form the spindle structure in the order of $\text{Te} > \text{Sb} > \text{Ge}$. From our viewpoint that the spindle structure is the manifestation of the covalency of chemical bonding, Te contributes to covalency more than Sb or Ge, but less than C. The eigenvalue and eigenvector maps for the other GST molecules, which are found in the supplementary material (Fig. S2), also support this ordering.

In Fig. 4, we plot τ_e^{S33} at the Lagrange point against the bond distance for all the GST molecules. The original data are found in Table 1. We see that $\tau_e^{S33} > 0$ for the Te-Te bonds and $\tau_e^{S33} < 0$ for the Ge-Ge bonds. As for the Sb-Sb bonds, τ_e^{S33} can be both positive and negative, and absolute values are smaller than those of the Ge-Ge and Te-Te bonds. τ_e^{S33} of the Ge-Sb bonds exhibit intermediate values between the Ge-Ge and Sb-Sb bonds, and similarly for the Ge-Te and Sb-Te bonds. Therefore, Fig. 4 can be interpreted that the GST atoms contribute to the positivity of the τ_e^{S33} at the Lagrange point in the order of $\text{Te} > \text{Sb} > \text{Ge}$, which is consistent with the tendency to form the spindle structure as mentioned above.

We next examine the differential eigenvalues of the electronic stress tensor at the Lagrange points. In Fig. 5 (a), we show a scatter plot of $\tau_e^{S33} - \tau_e^{S22}$ and $\tau_e^{S22} - \tau_e^{S11}$ for GST bonds, and, in Fig. 5 (b), we in addition plot points for the hydrocarbon molecules, Li clusters, and Na clusters, which are taken from the data set studied in our previous paper [42]. We see that both $\tau_e^{S33} - \tau_e^{S22}$ and $\tau_e^{S22} - \tau_e^{S11}$ of the Li and Na clusters are $O(10^{-4})$. As for the GST molecules, $\tau_e^{S33} - \tau_e^{S22}$ is $O(10^{-2})$, which is somewhat larger than $\tau_e^{S22} - \tau_e^{S11}$, which is $O(10^{-4})$ - $O(10^{-3})$. As for the hydrocarbon molecules, $\tau_e^{S33} - \tau_e^{S22}$ is $O(10^{-1})$ and this is much larger than $\tau_e^{S22} - \tau_e^{S11}$. Thus, the degree of degeneracy can be summarized as $\text{Li, Na} \ll \text{GST} \ll \text{h/c}$. This is consistent with the usual classification of Ge, Sb and Te as metalloids,

which are placed in between metals and non-metals. Further research may reveal that the electronic stress tensor density provides a new criterion to define metalloids based on the electronic structures.

Incidentally, we compute the electronic stress tensor of Ge, Sb, and Te crystals using periodic models. We compute the electronic stress tensor at the midpoint of two nearest neighborhood atoms (it is the Lagrange point by symmetry). The results are summarized in Table 2 and plotted in Figs. 4 and 5 (a). We see in Fig. 5 (a) that all the crystal structures have similar values of $\tau_e^{S33} - \tau_e^{S22}$ and $\tau_e^{S22} - \tau_e^{S11}$ to those of the GST molecules. This indicates that the degree of degeneracy does not differ much between the crystal structures and molecules. As for τ_e^{S33} , as shown in Fig. 4, all the crystal structures exhibit negative values of about -2×10^{-3} . This is close to the τ_e^{S33} of the Ge-Ge bonds in the molecules, but not to those of the Sb-Sb or Te-Te bonds, which, respectively, are negative with absolute values of $O(10^{-5})$ or positive with values of $O(10^{-3})$. Thus, from the viewpoint of the electronic stress tensor, the covalency of the chemical bonding involving Sb and Te atoms in the GST molecules does not appear in their crystal structures and some metallicity is manifested. In other words, while Ge, Sb and Te do not exhibit covalency in their crystal structure, Sb and Te show some covalency in their molecular structure.

4.3.3 Bond order and force constant

We briefly review our past works [32–34, 40] on our bond order b_ϵ (Eq. (46)), which is defined using concepts based on the Rigged QED. First, it has been pointed out [32] that b_ϵ of a single, double, and triple bond between carbon atoms in hydrocarbons is close to 1, 2 and 3 respectively, consistent with a conventional bond order. Also, b_ϵ of the C-C bond in a benzene molecule is close to 1.5. However, it has been also reported that b_ϵ of some diatomic molecules overestimate or underestimate the conventional bond order, e.g., b_ϵ of N_2 is 7.462. Then, in Ref. [33], the correlation between b_ϵ and bond distance r_e has been investigated using various simple organic compounds. By comparing with other bond orders proposed in the literature, b_ϵ is found to have a comparable or better correlation. This has been also shown using hydrogenated Pt [34] and Pd [40] clusters. We, however, have not investigated a correlation between b_ϵ and a quantity related to energy. Therefore, we here compute the bond dissociation energy B and force constant k of the GST bonds, and investigate the correlations with b_ϵ .

The results are summarized in Table 3. k is calculated based on the directional derivative of a total energy E of a molecule with respect to the bond direction $\vec{s}$. Namely, it is computed using force constant matrix $\frac{\partial^2 E}{\partial x^i \partial x^j}$ as

$$k = -\frac{\partial^2 E}{\partial \vec{s} \partial \vec{s}} = -\sum_{i,j=1}^3 s^i \frac{\partial^2 E}{\partial x^i \partial x^j} s^j. \quad (47)$$

The scatter plots of b_ϵ versus r_e , B , and k are shown in Fig. 6. We can see that b_ϵ is negatively correlated with r_e and positively correlated with k and B , consistently with the usual notion of bond order. In fact, their correlation coefficients are -0.968 , 0.570 , and 0.910 , respectively for r_e , B , and k . Since we need to know the energy when two fragments of a molecule are infinitely apart to compute B , it is reasonable not to find a strong correlation between b_ϵ and B . Note that b_ϵ is defined only using the quantities at the equilibrium structure. On the other hand, the reason why the correlation with k is very strong may be understood as follows.

The meaning of k , often called a spring constant, is how much energy we need to stretch the bond by an infinitesimal distance. It can be expressed as $k\delta^2/2$, where δ denotes the infinitesimal displacement. We may interpret this energy using our energy density $\varepsilon_\tau^S(\vec{r})$ (Eq. (45)) and the “Lagrange surface” [11, 12] which is defined as a separatrix in the tension density $\vec{\tau}^S(\vec{r})$ (Eq. (40)). The vector field of $\vec{\tau}^S(\vec{r})$ generally has a pattern in which vectors originate from atomic nuclei, and they collide to form separatrix. See Figs. 2 (b) or 7 (a). We call this separatrix the Lagrange surface and regard it as the boundary of atoms in a molecule. In Fig. 7 (a), we show some examples of the Lagrange surface in

a $\text{GeH}_3\text{-SbH}_2$ molecule. When we move apart two atoms bounded by the Lagrange surface for a small distance, it may be reasonable to suppose the required energy to be proportional to the energy stored in the Lagrange surface, that is, $\int_S \varepsilon_\tau^S(\vec{\sigma}) d^2\sigma$, where the integration is taken over the Lagrange surface S . To support this idea, we compute an alternative bond order [39, 40] defined as

$$b_{\varepsilon(S)} = \frac{\int_{S_{AB}} \varepsilon_\tau^S(\vec{\sigma}) d^2\sigma}{\int_{S_{HH}} \varepsilon_\tau^S(\vec{\sigma}) d^2\sigma}, \quad (48)$$

where S_{AB} denotes the Lagrange surface between atoms A and B, and investigate the correlation with k (Fig. S3 (c)). The correlation coefficient is found to be 0.887, and the linear fit $y = ax + b$, where x and y , respectively, represent k and $b_{\varepsilon(S)}$, gives $a = 5.54$ and $b = 5.62 \times 10^{-3}$. (The value of $b_{\varepsilon(S)}$ for each bond is summarized in Table 3.) This suggests that $k \propto \int_S \varepsilon_\tau^S(\vec{\sigma}) d^2\sigma$ holds to a large extent. As for the linear fit for b_ε against k , we obtain $a = 1.63$ and $b = -7.54 \times 10^{-3}$. Since b is close to zero for both cases, we can approximately consider $b_{\varepsilon(S)} \propto b_\varepsilon$ with a proportional constant of 3.4 (the ratio of a 's) for these GST bonds. This relation between $b_{\varepsilon(S)}$ and b_ε can be confirmed directly by computing $b_{\varepsilon(S)}/b_\varepsilon$ for each GST bond which is shown in Fig. 8. The average of $b_{\varepsilon(S)}/b_\varepsilon$ over 35 bonds is 3.74 with the standard deviation of 0.21. Since the standard deviation is relatively small (5.6% of the average), we may regard $b_{\varepsilon(S)} \propto b_\varepsilon$ for these bonds. The values of the proportional constant derived in two ways are consistent.

This relation, that $b_{\varepsilon(S)}$ of the GST bonds is approximately obtained by multiplying b_ε by a common factor, holds if the integration of $\varepsilon_\tau^S(\vec{r})$ over their Lagrange surface is well approximated by $\varepsilon_\tau^S(\vec{r}_L)$ multiplied by a common factor. Such an assumption can be valid, if the Lagrange surfaces of the GST bonds are flat and the energy density distributions on them are expressed by Gaussian functions with a common value of the exponent. We can see this is roughly true as follows. First, the flatness can be checked by the visual inspection of the Lagrange surface (Fig. 7 (a) and Fig. S2 in the supplementary material). Then, we plot $\varepsilon_\tau^S(\vec{r})$ against the distance from $\vec{r}_L$ for the points which constitute the Lagrange surface. The example of this plot for the $\text{GeH}_3\text{-SbH}_2$ molecule is found in Fig. 7 (b). Actually, we plot $\varepsilon_\tau^S(\vec{r})$ divided by the energy density of a hydrogen molecule at its Lagrange point so that the value at $\vec{r}_L$ (*i.e.* $|\vec{r} - \vec{r}_L| = 0$) becomes b_ε . In the figure, we also plot the result of the fit to the Gaussian function $b_\varepsilon \exp\{-\alpha|\vec{r} - \vec{r}_L|^2\}$ where the exponent α is the fitting parameter. The figure shows that $\varepsilon_\tau^S(\vec{r})/\varepsilon_{\tau\text{HH}}^S(\vec{r}_L)$ is well fitted by the Gaussian function with $\alpha = 1.32$. We perform such a fit to all the GST bonds (Figures similar to Fig. 7 (b) are plotted in Fig. S4. The values of α are summarized in Table 3 and Fig. S5) and the average and standard deviation of the exponent are computed to be 1.31 and 9.40×10^{-2} , respectively. Therefore, as for the GST bonds, we can say that the energy density distribution over the Lagrange surface is expressed by the Gaussian functions with a common exponent, which leads to $\int_S \varepsilon_\tau^S(\vec{\sigma}) d^2\sigma \propto \varepsilon_\tau^S(\vec{r}_L)$.

As a further test for the idea that $b_{\varepsilon(S)}$ is proportional to the force constant, we examine homonuclear diatomic molecules, from H_2 to I_2 excluding the group 18 elements. We use experimental values for r_e , B , and k as is summarized in Table 4. B is the energy of the ground state atomic products relative to the lowest existing level of the molecule, often denoted by D_0 . k is converted from the frequency ω (which is also shown in the table) via $k = M\omega^2/2$, where M is the atomic mass. Note that some of the experimental values are not available or controversial and we use computational values in such cases. We adopt computational values for r_e and ω of Ga_2 from Ref. [65], and r_e and ω of In_2 from Ref. [70]. b_ε and $b_{\varepsilon(S)}$ are computed with the same setups as the GST bonds, and shown in Table 4. We first study how much b_ε is correlated with r_e , B , and k . The correlation coefficients are found to be -0.583 , 0.834 , and 0.978 , respectively for r_e , B , and k , showing very strong correlation between b_ε and k as is the case with the GST bonds. As for $b_{\varepsilon(S)}$, the correlation with k is also very strong, with the correlation coefficient 0.990 . The scatter plots of k versus b_ε and $b_{\varepsilon(S)}$ are shown in Fig 9 (a) and (b) respectively, and we can see these strong correlations (similar scatter plots for r_e and B are shown in Figs. S6 and S7). However, one may notice a difference between Fig 9 (a) and (b) that the panel (b)

shows more proportionality than the panel (a). In fact, while the linear fit $b_\epsilon = a_1 k + b_1$ gives $a_1 = 3.12$ and $b_1 = -0.23$, $b_{\epsilon(S)} = a_2 k + b_2$ gives $a_2 = 3.64$ and $b_2 = 5.87 \times 10^{-3}$. Since b_1 is not negligible, b_ϵ is hardly considered to be proportional to k , whereas very small value of b_2 implies that $b_{\epsilon(S)} \propto k$ holds to a large extent. Therefore, in general, $b_{\epsilon(S)}$ is a better descriptor of a chemical bond than b_ϵ . The drawback is that, since the computation of $b_{\epsilon(S)}$ involves the integration over the Lagrange surface, it costs much greater than that of b_ϵ .

Finally, some comments on the correlations of r_e and B with our bond orders are in order. First, the correlation coefficient between r_e and b_ϵ is -0.968 for the GST molecules and -0.583 for the homonuclear diatomic molecules. (As for $b_{\epsilon(S)}$, they are -0.970 and -0.651 , respectively.) The difference can be attributed to the fact that the GST data consists of similar chemical bonds formed by Ge, Sb, and Te, whereas the homonuclear diatomic molecule data contains various types of elements. It has been found that b_ϵ correlates well with r_e , as mentioned in the beginning of this subsection, but it has been also shown that the slope on the r_e - b_ϵ plane depends on the type of chemical bonding. For example, in Ref. [40], the Pd-Pd bonds and Pd-H bonds are found to have different slopes. Also, among the Pd-H bonds, the bonds with shorter bond length ($\lesssim 1.9$ Å) have steeper slope than those with longer bond length. Therefore, when a data contains different types of chemical bonding, even though r_e and b_ϵ exhibit negative correlation, the correlation coefficient tends to be somewhat away from -1 . Second, the correlation coefficient between B and b_ϵ is 0.570 for the GST data and 0.834 for the homonuclear diatomic molecules data. (As for $b_{\epsilon(S)}$, they are 0.569 and 0.906 respectively.) There is again some notable difference between the two data sets. Since the correlation coefficients between b_ϵ and k are close to 1 for both data sets, the degrees of correlation between B and b_ϵ are roughly equal to those between B and k . Although B and k are likely to be positively correlated, since they are not linear to each other in general, we do not expect a very strong correlation between B and k . Then, the relatively low value of correlation coefficient of the GST data is reasonable while that of the homonuclear diatomic molecules data is unexpectedly high. The latter may be understood by a universality of potential energy curve for diatomic molecules (e.g. [75–77]), which has been studied for a long time. It is, however, an empirical relation at this stage and the discussion of its relevance here is beyond the scope of this paper.

4.4 Conclusions

We have analyzed the electronic structure of 35 molecules which may exist in gas phase of CVD process for GeSbTe alloy using the electronic stress tensor, with special focus on the chemical bonds between Ge, Sb and Te atoms. Our study consists of two parts. First, we have studied the pattern of the eigenvalues and eigenvectors of the electronic stress tensor density of the GST bonds. Next, we have computed the bond order which is defined by the stress-tensor-based energy density for the GST bonds, and have investigated the correlation with the energy-related quantities such as the bond dissociation energy and force constant.

In the first part, we have found that, from the viewpoint of the electronic stress tensor density, GST bonds exhibit intermediate properties between alkali metals and hydrocarbon molecules. This is illustrated by the sign and degeneracy pattern of the three eigenvalues of the electronic stress tensor density at the Lagrange point between two atoms. In our previous studies, we have pointed out that the negative and degenerate eigenvalues, which indicate a lack of directionality with the compressive stress, characterize some aspects of metallicity of chemical bonding. By contrast, the positive largest eigenvalue and much smaller negative other two eigenvalues, which indicates a solid directionality with the tensile stress in that direction, characterize covalency. The former pattern has been typically found in the alkali metals and the latter in the hydrocarbon molecules. Our results in the present paper suggest that the GST bonds can be located in between metallic bonding and covalent bonding in terms of their electronic stress tensor. This is consistent with the usual classification of Ge, Sb and Te as metalloids, which have intermediate properties between metals and nonmetals.

In the second part, we have found that the correlation of our bond order with the bond dissociation

energy is not so strong, while one with the force constant is very strong. We have interpreted this results in terms of the energy density on the “Lagrange surface”, which is considered to define the boundary surface of atoms in a molecule in the framework of the electronic stress tensor analysis. In this study, we have found that both of our definitions of bond order b_ϵ and $b_{\epsilon(S)}$, where the former uses the energy density at the Lagrange point while the latter involves the integration over the Lagrange surface, have strong correlation with the force constant. We have argued that, if the interpretation above is correct, $b_{\epsilon(S)}$ is the one which is more directly connected with the force constant, and the strong correlation of the force constant with b_ϵ follows from that with $b_{\epsilon(S)}$. In fact, we have shown that $b_{\epsilon(S)}/b_\epsilon$ does not vary much among the GST bonds, which originate from the fact that the energy distributions on the Lagrange surface of the GST bonds can be well expressed by Gaussian functions centered at the Lagrange point and with a common value of the exponent. As the results of this study, it is hinted that the stress-tensor-based energy density can be related not only to the total energy but also to the force constant by combining with another Rigged QED concept, the Lagrange surface.

In our future work, regarding the first part, we wish to apply the electronic stress tensor analysis to the other elements which are conventionally classified as metalloids, B, Si and As, to see whether it can provide a criterion to define metalloids. For that purpose, it is also necessary to extend the analysis to the elements nearby metalloids in the periodic table. We also wish to apply the electronic stress tensor analysis to transition metals, ionic bonds, hypervalency, and so on, to strengthen its usefulness. It would enable us to deepen our understanding of the nature of chemical bonding. As for the second part, a further direction of the study will be to provide more evidence for our results by using other types of molecules. If the relation concerning the force constant, which is an experimental observable derived from a vibrational spectrum, is established in general, it would help to solidify such ideas as the stress-tensor-based energy density and Lagrange surface. In the end, we would like to emphasize that our studies are based on the quantities defined at each point in space, which originate from the quantum field theoretic consideration and not from the electron density. We believe that our method will lead us to new and beneficial views on chemical systems.

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Table 1: Data for the bonds between Ge, Sb, and Te atoms in the GST molecules. r_e is the bond distance. τ_e^{S33} , τ_e^{S22} , and τ_e^{S11} are three eigenvalues of the electronic stress tensor density at the Lagrange point.

Molecule	r_e [Å]	$\tau_e^{S33}(\times 10^3)$	$\tau_e^{S22}(\times 10^3)$	$\tau_e^{S11}(\times 10^3)$
GeH ₂ -GeH ₂	2.343	-7.533	-18.29	-20.08
GeH ₂ (tBu)-GeH ₂ (tBu)	2.489	-1.811	-16.21	-16.31
GeH ₃ -GeH ₂	2.489	-1.768	-15.71	-15.95
GeH ₃ -GeH ₂ (tBu)	2.486	-1.841	-16.23	-16.28
GeH ₃ -GeH ₃	2.483	-1.861	-16.25	-16.25
SbH ₂ -SbH ₂	2.948	0.136	-9.121	-9.562
SbH(iPr)-SbH ₂	2.946	0.053	-9.204	-9.654
SbH(iPr)-SbH(iPr)	2.937	-0.061	-9.392	-9.891
Sb(iPr) ₂ -SbH ₂	2.944	0.022	-9.335	-9.724
Sb(iPr) ₂ -SbH(iPr)	2.939	-0.055	-9.451	-9.897
Sb(iPr) ₂ -Sb(iPr) ₂	2.954	0.213	-9.226	-9.752
TeH-TeH	2.854	1.897	-12.43	-12.45
Te(iPr)-TeH	2.844	1.514	-12.69	-12.82
Te(iPr)-Te(iPr)	2.831	1.139	-13.03	-13.24
GeH ₂ -SbH ₂	2.703	-0.940	-12.04	-12.61
GeH ₂ -SbH(iPr)	2.696	-1.102	-12.15	-12.83
GeH ₂ -Sb(iPr) ₂	2.692	-1.218	-12.25	-12.99
GeH ₂ (tBu)-SbH ₂	2.703	-0.860	-12.49	-12.86
GeH ₂ (tBu)-SbH(iPr)	2.702	-0.894	-12.59	-12.97
GeH ₂ (tBu)-Sb(iPr) ₂	2.704	-0.869	-12.58	-13.01
GeH ₃ -SbH ₂	2.700	-0.811	-12.52	-12.82
GeH ₃ -SbH(iPr)	2.694	-0.995	-12.70	-13.04
GeH ₃ -Sb(iPr) ₂	2.696	-0.987	-12.69	-13.07
GeH ₂ (tBu)-Te(iPr)	2.654	0.059	-14.36	-15.28
GeH ₂ (tBu)-TeH	2.658	0.134	-14.05	-15.15
GeH ₂ -TeH	2.653	-0.649	-13.82	-15.08
GeH ₂ -Te(iPr)	2.637	-1.078	-14.32	-15.57
GeH ₃ -TeH	2.649	0.209	-14.28	-15.30
GeH ₃ -Te(iPr)	2.636	-0.183	-14.76	-15.75
SbH ₂ -TeH	2.892	0.838	-10.60	-11.12
SbH ₂ -Te(iPr)	2.874	0.343	-11.05	-11.52
SbH(iPr)-TeH	2.890	0.627	-10.59	-11.28
SbH(iPr)-Te(iPr)	2.878	0.441	-10.97	-11.58
Sb(iPr) ₂ -TeH	2.892	0.410	-10.66	-11.20
Sb(iPr) ₂ -Te(iPr)	2.879	0.338	-11.05	-11.53

Table 2: Data for the bonds in the crystal structure of Ge, Sb, and Te. r_e is the distance between the nearest neighborhood atoms. τ_e^{S33} , τ_e^{S22} , and τ_e^{S11} are three eigenvalues of the electronic stress tensor density at the Lagrange point.

Crystal	r_e [Å]	$\tau_e^{S33} (\times 10^3)$	$\tau_e^{S22} (\times 10^3)$	$\tau_e^{S11} (\times 10^3)$
Ge	2.450	-2.612	-19.52	-19.52
Sb	2.907	-1.981	-12.12	-12.23
Te	2.835	-1.712	-17.46	-17.81

Table 3: Data for the bonds between Ge, Sb, and Te atoms in the GST molecules. B and k are respectively the bond dissociation energy and force constant. b_ϵ and $b_{\epsilon(S)}$ are our bond orders (Eqs. (46) and (48)). α is a fitting parameter for the energy density distribution on the Lagrange surface (see the text for the details).

Molecule	B [kcal/mol]	k [a.u.]	b_ϵ	$b_{\epsilon(S)}$	α
GeH ₂ -GeH ₂	40.40	0.122	0.179	0.648	1.561
GeH ₂ (tBu)-GeH ₂ (tBu)	59.79	0.080	0.132	0.485	1.443
GeH ₃ -GeH ₂	40.30	0.079	0.128	0.473	1.444
GeH ₃ -GeH ₂ (tBu)	59.86	0.082	0.132	0.484	1.448
GeH ₃ -GeH ₃	59.58	0.083	0.132	0.482	1.455
SbH ₂ -SbH ₂	32.21	0.058	0.071	0.284	1.186
SbH(iPr)-SbH ₂	32.62	0.056	0.072	0.291	1.175
SbH(iPr)-SbH(iPr)	33.09	0.060	0.074	0.301	1.177
Sb(iPr) ₂ -SbH ₂	32.72	0.056	0.073	0.297	1.166
Sb(iPr) ₂ -SbH(iPr)	33.19	0.056	0.075	0.303	1.174
Sb(iPr) ₂ -Sb(iPr) ₂	31.05	0.056	0.072	0.294	1.164
TeH-TeH	33.24	0.064	0.088	0.288	1.279
Te(iPr)-TeH	34.86	0.063	0.092	0.307	1.278
Te(iPr)-Te(iPr)	35.32	0.066	0.097	0.327	1.285
GeH ₂ -SbH ₂	28.06	0.069	0.098	0.378	1.323
GeH ₂ -SbH(iPr)	28.94	0.068	0.100	0.390	1.316
GeH ₂ -Sb(iPr) ₂	30.10	0.069	0.102	0.396	1.317
GeH ₂ (tBu)-SbH ₂	45.95	0.060	0.101	0.389	1.314
GeH ₂ (tBu)-SbH(iPr)	45.75	0.060	0.102	0.395	1.309
GeH ₂ (tBu)-Sb(iPr) ₂	46.22	0.062	0.102	0.398	1.298
GeH ₃ -SbH ₂	45.13	0.063	0.100	0.385	1.323
GeH ₃ -SbH(iPr)	45.72	0.064	0.103	0.399	1.318
GeH ₃ -Sb(iPr) ₂	45.95	0.065	0.103	0.401	1.309
GeH ₂ (tBu)-Te(iPr)	49.93	0.064	0.114	0.404	1.357
GeH ₂ (tBu)-TeH	52.67	0.064	0.112	0.415	1.355
GeH ₂ -TeH	33.96	0.075	0.114	0.403	1.393
GeH ₂ -Te(iPr)	33.70	0.077	0.119	0.428	1.391
GeH ₃ -TeH	50.13	0.069	0.113	0.404	1.375
GeH ₃ -Te(iPr)	49.04	0.071	0.118	0.427	1.375
SbH ₂ -TeH	35.71	0.061	0.080	0.289	1.246
SbH ₂ -Te(iPr)	34.54	0.052	0.085	0.310	1.260
SbH(iPr)-TeH	38.52	0.061	0.082	0.297	1.236
SbH(iPr)-Te(iPr)	37.04	0.061	0.085	0.297	1.233
Sb(iPr) ₂ -TeH	39.79	0.048	0.082	0.301	1.239
Sb(iPr) ₂ -Te(iPr)	38.36	0.060	0.085	0.319	1.233

Table 4: Data for the homonuclear diatomic molecules. r_e , ω , and B are respectively the bond distance, frequency, and dissociation energy, whose values are taken from the references. The force constant k is converted from ω . Details are found in the text. b_ε and $b_{\varepsilon(S)}$ are our bond orders (Eqs. (46) and (48)).

Molecule	r_e [Å]	ω [cm ⁻¹]	k [a.u.]	B [kcal/mol]	References	b_ε	$b_{\varepsilon(S)}$
H ₂	0.74144	4401.21	0.367	103.26	[62]	1.000	1.000
Li ₂	2.6729	351.43	0.016	24.2	[62]	0.013	0.112
Be ₂	2.453	270.7	0.012	2.308	[63, 64]	0.035	0.165
B ₂	1.590	1051.3	0.230	69	[62]	0.452	1.205
C ₂	1.2425	1854.71	0.781	143	[62]	2.349	3.542
N ₂	1.09769	2358.57	1.474	225.0	[62]	5.849	6.437
O ₂	1.20752	1580.19	0.756	118.0	[62]	3.229	4.079
F ₂	1.41193	916.64	0.302	36.94	[62]	1.303	1.425
Na ₂	3.0789	159.125	0.011	16.6	[62]	0.006	0.065
Mg ₂	3.891	51.12	0.001	1.16	[62]	0.004	0.022
Al ₂	2.466	350.01	0.063	37	[62]	0.074	0.374
Si ₂	2.246	510.98	0.138	74.0	[62]	0.245	0.802
P ₂	1.8934	780.77	0.358	116.1	[62]	0.650	1.701
S ₂	1.8892	725.65	0.319	100.76	[62]	0.701	1.513
Cl ₂	1.988	559.78	0.208	57.1742	[62]	0.421	0.645
K ₂	3.9051	92.021	0.006	11.9	[62]	0.004	0.044
Ca ₂	4.2773	64.93	0.003	3.0	[62]	0.004	0.038
Ga ₂	2.746	162	0.034	26.36	[65, 66]	0.042	0.133
Ge ₂	2.3680	287.9	0.116	65	[62, 67]	0.122	0.478
As ₂	2.1026	429.55	0.262	91.3	[62]	0.423	1.286
Se ₂	2.166	385.303	0.225	78.66	[62]	0.379	1.015
Br ₂	2.2811	325.321	0.158	45.444	[62]	0.246	0.540
Rb ₂	4.2099	57.781	0.005	11	[62, 68]	0.004	0.042
Sr ₂	4.67174	40.32831	0.003	3.036	[69]	0.003	0.031
In ₂	3.14	111	0.027	17.8	[70, 71]	0.034	0.170
Sn ₂	2.746	189.74	0.082	43.8300	[72, 73]	0.108	0.499
Sb ₂	2.476	269.623	0.167	69.0672	[74]	0.220	0.869
Te ₂	2.5574	247.07	0.150	61.73	[62]	0.195	0.678
I ₂	2.666	214.50	0.111	35.5672	[62]	0.137	0.385

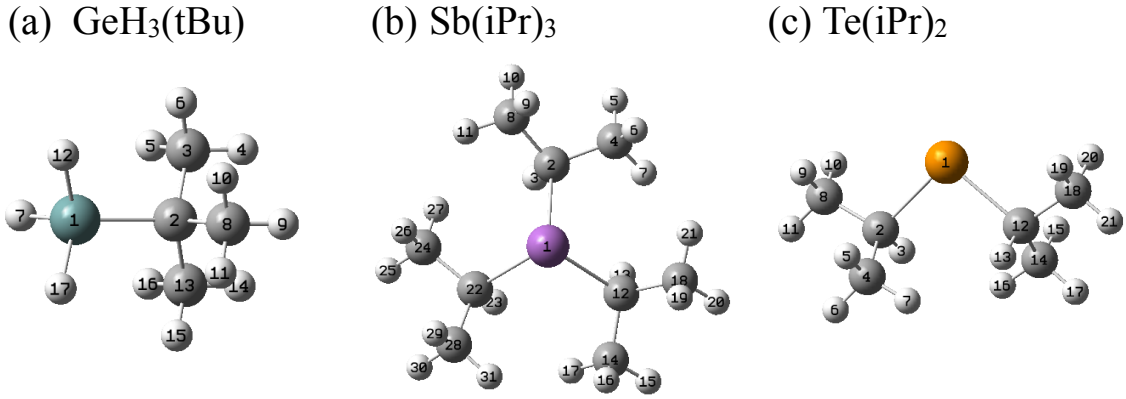


Fig. 1: The optimized structures of the precursors: (a) $\text{GeH}_3(\text{tBu})$ (C_{3v}), (b) $\text{Sb}(\text{iPr})_3$ (C_3), and (c) $\text{Te}(\text{iPr})_2$ (C_2).

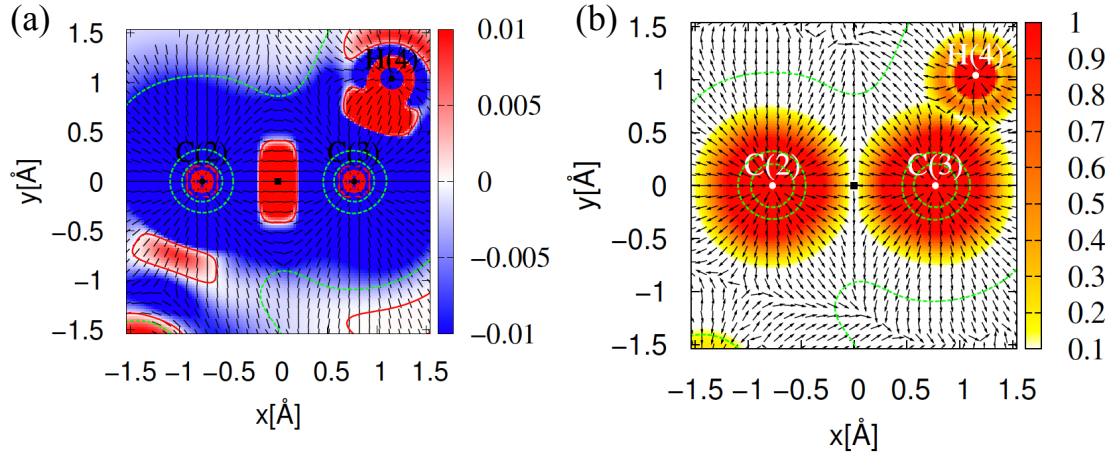


Fig. 2: The largest eigenvalue of the electronic stress tensor density (color map) and corresponding eigenvector (black rods) are shown in panel (a), and tension density (black arrows) and its norm (color map) are shown in panel (b), around a C-C bond in $\text{GeH}_3(\text{tBu})$. In both panels, the electronic interface is depicted by the green dashed lines, and the Lagrange point is shown by a black square. In panel (a), the red solid lines show the zero contour lines of the eigenvalue.

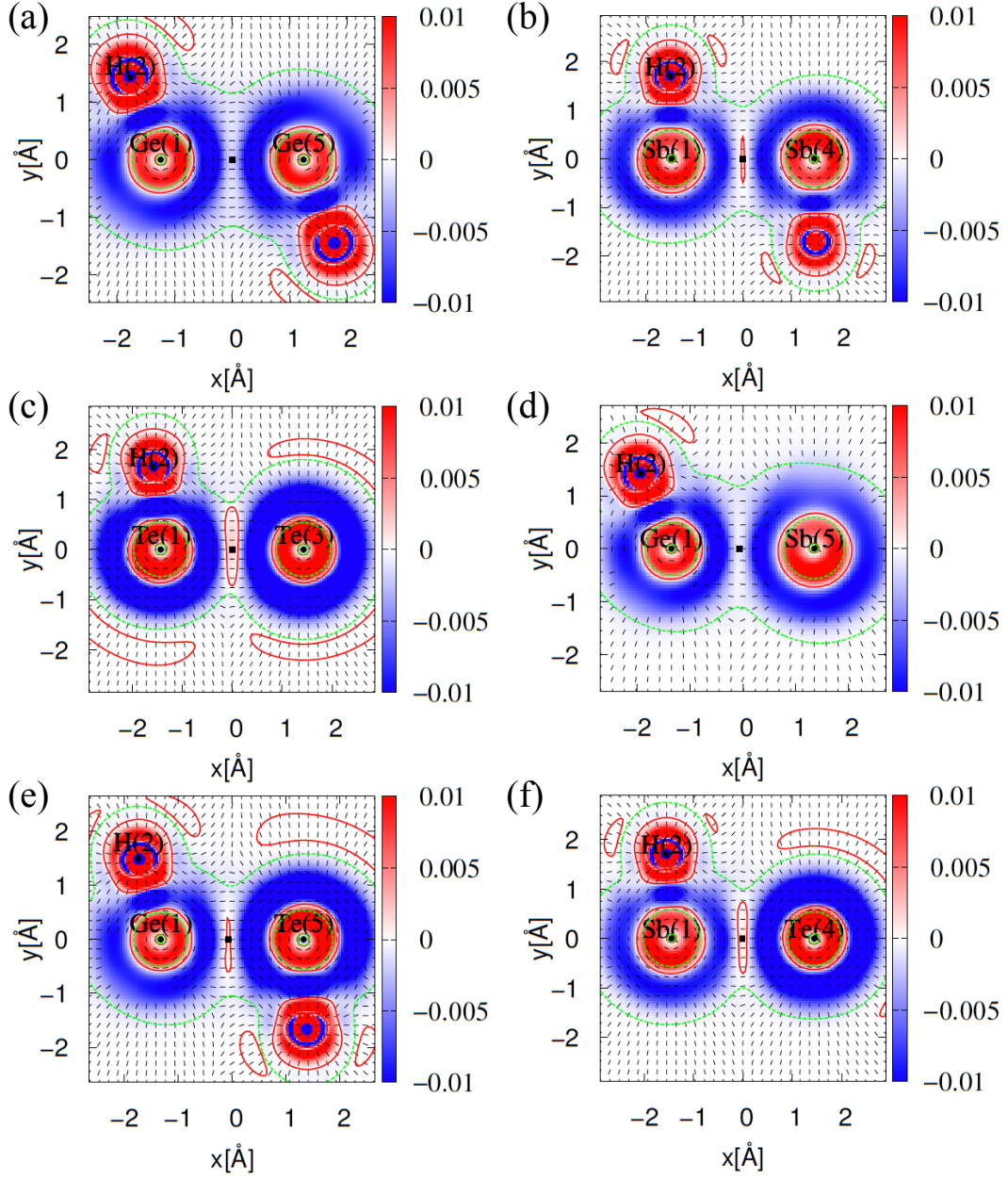


Fig. 3: The largest eigenvalue of the electronic stress tensor density and corresponding eigenvector between the GST atoms are shown in the same manner as Fig. 2 (a). (a) $\text{GeH}_3\text{-GeH}_3$, (b) $\text{SbH}_2\text{-SbH}_2$, (c) TeH-TeH , (d) $\text{GeH}_3\text{-SbH}_2$, (e) $\text{GeH}_3\text{-TeH}$, and (f) $\text{SbH}_2\text{-TeH}$.

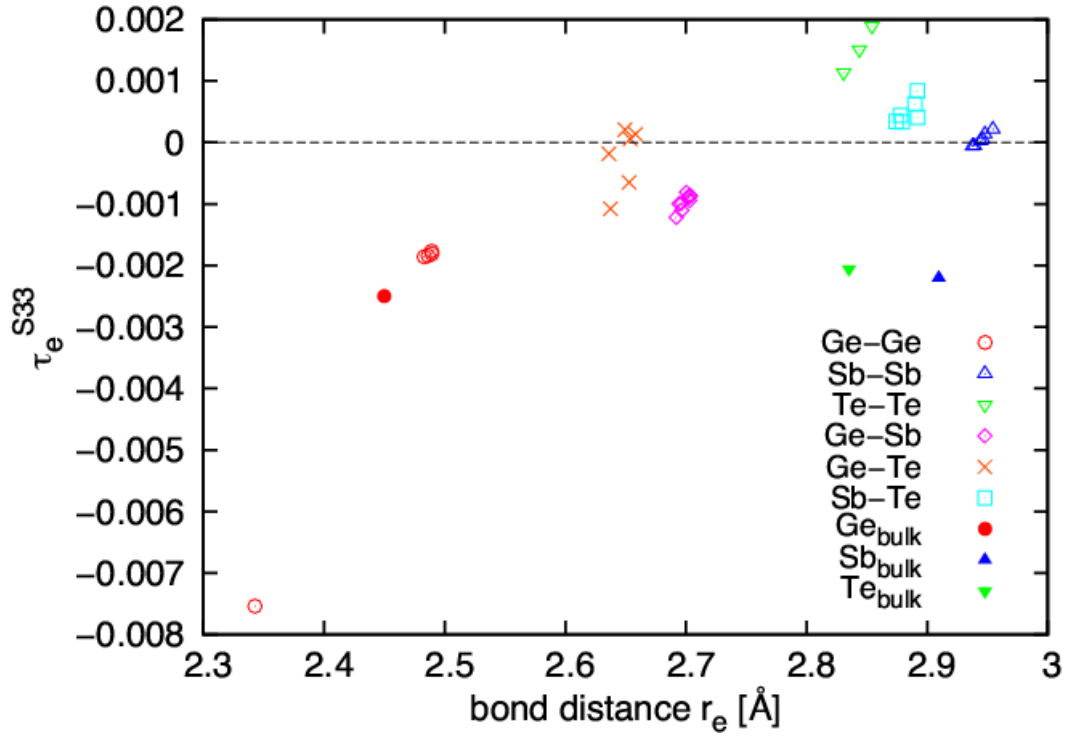


Fig. 4: The relation between bond distance and the largest eigenvalue of the electronic stress tensor at the Lagrange point. The labels with “bulk” in the subscripts denote that they are computed for the crystal structures.

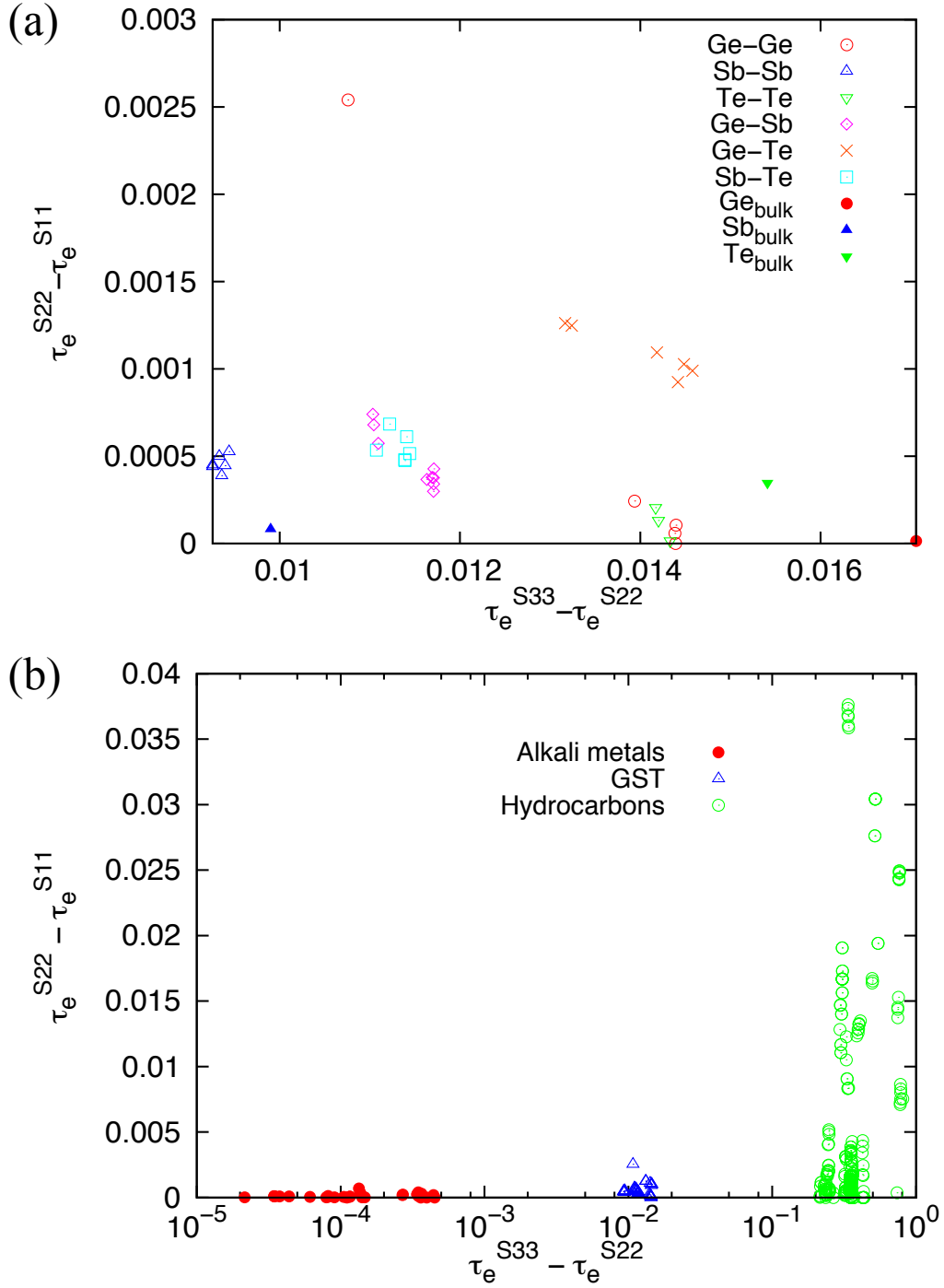


Fig. 5: Differential eigenvalues of the electronic stress tensor at the Lagrange point. In the panel (a), labels with “bulk” in the subscripts denote that they are computed for the crystal structures.

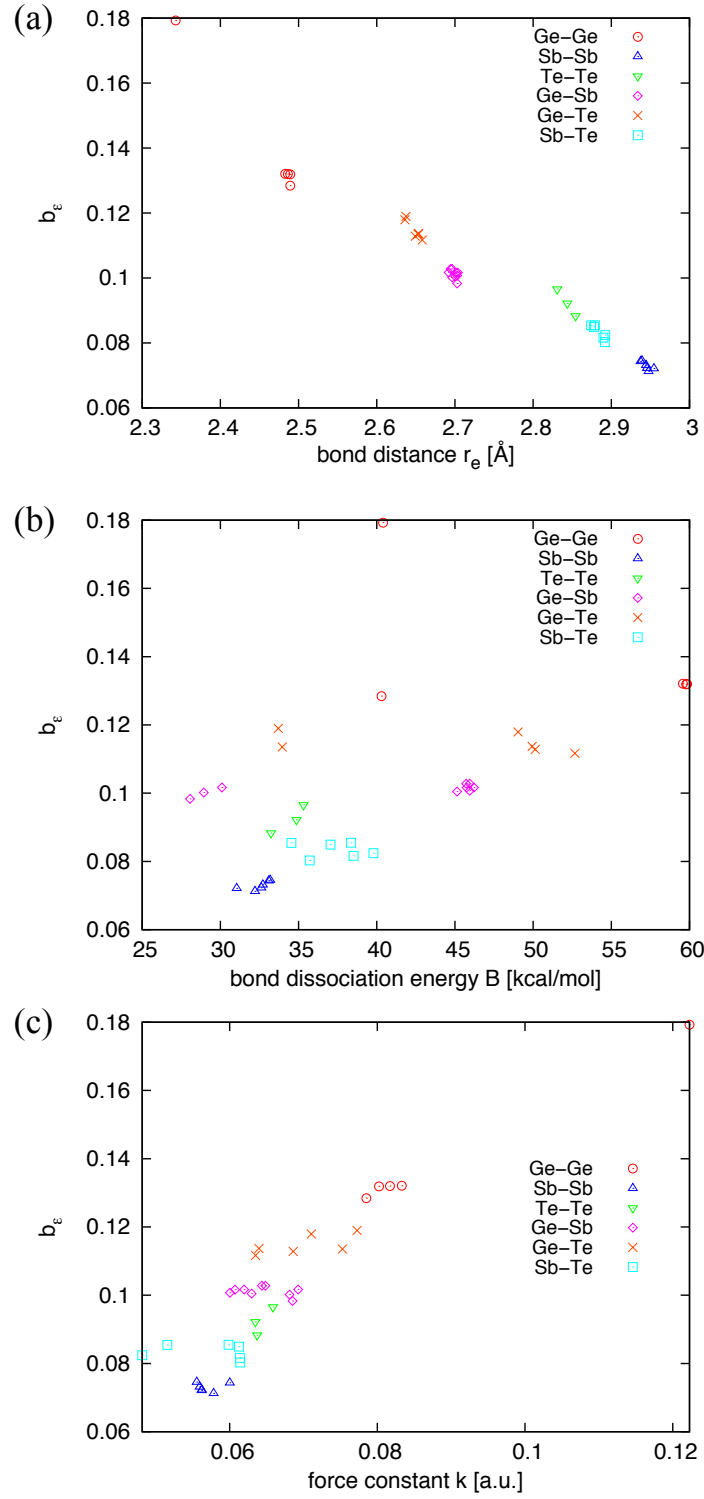


Fig. 6: The relation between energy density based bond order b_e and (a) bond distance, (b) dissociation energy, and (c) force constant, for the GST bonds.

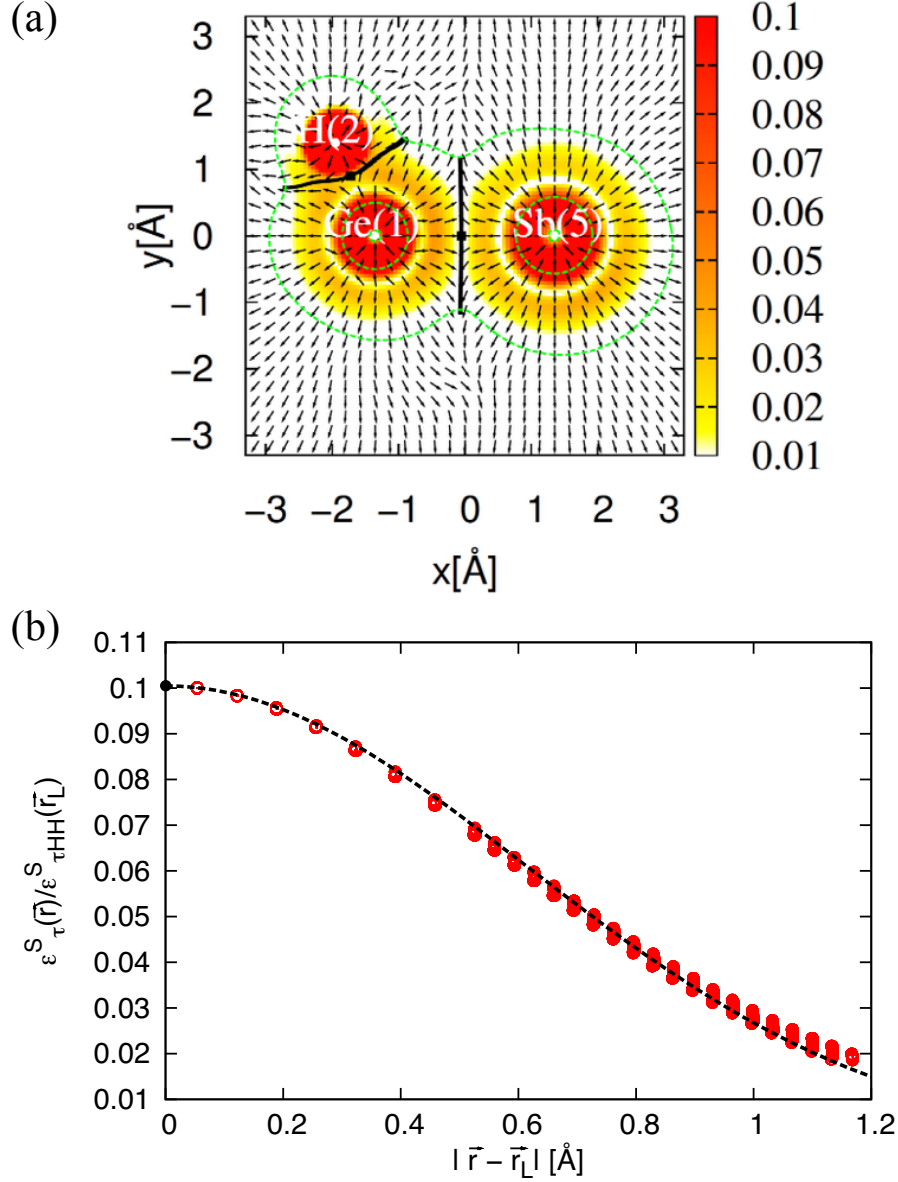


Fig. 7: In panel (a), the tension density is plotted similarly to Fig. 2 (b) for the Ge-Sb bond in a $\text{GeH}_3\text{-SbH}_2$ molecule. The Lagrange surfaces are shown by black solid lines and the Lagrange points by black squares. In panel (b), the energy density distribution on the Lagrange surface between the Ge and Sb atoms is plotted as a function of the distance from the Lagrange point. The energy density is normalized by the energy density of a H_2 molecule at its Lagrange point. The black dashed line is the best fit Gaussian function: $b_\epsilon \exp \{-\alpha |\vec{r} - \vec{r}_L|^2\}$ where $\alpha = 1.32$.

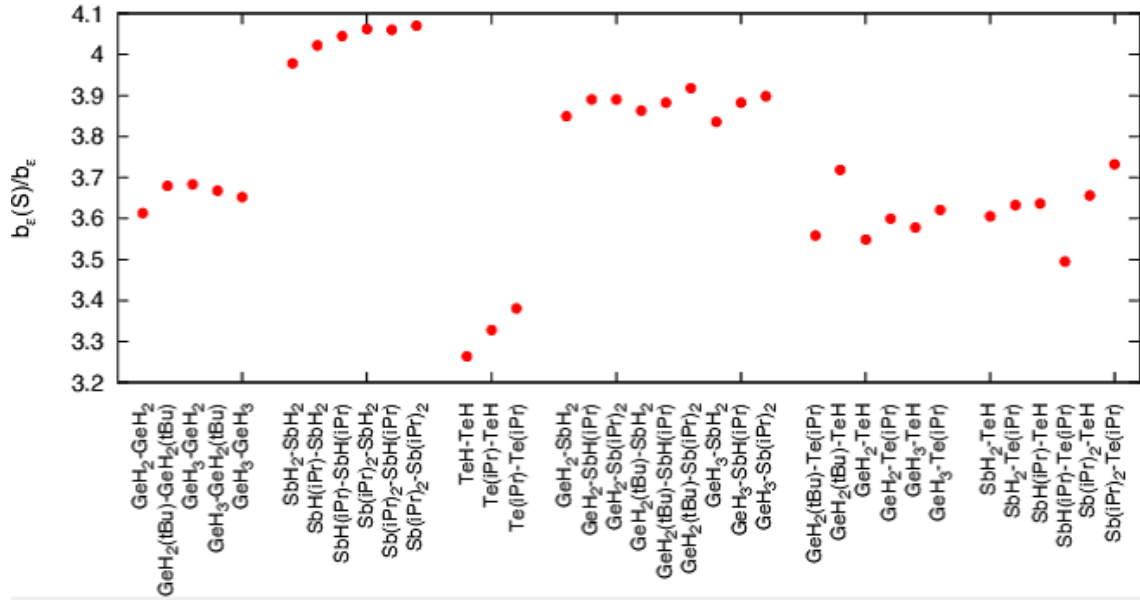


Fig. 8: The ratio of $b_{\epsilon(S)}$ to b_{ϵ} for the GST bonds.

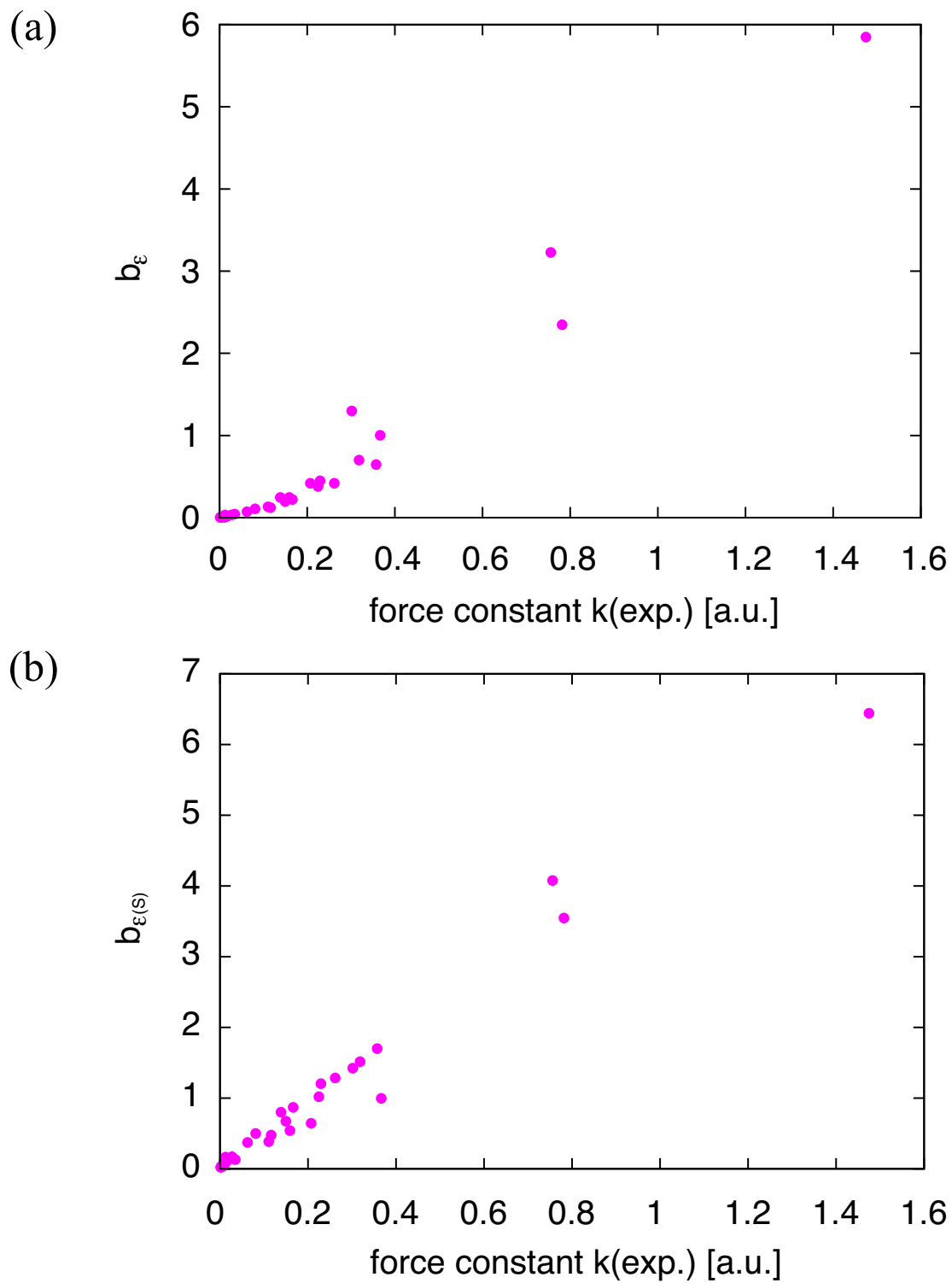


Fig. 9: The relation between force constant k and (a) b_ϵ and (b) $b_{\epsilon(s)}$, for the bonds in the homonuclear diatomic molecules.

Supplementary Data

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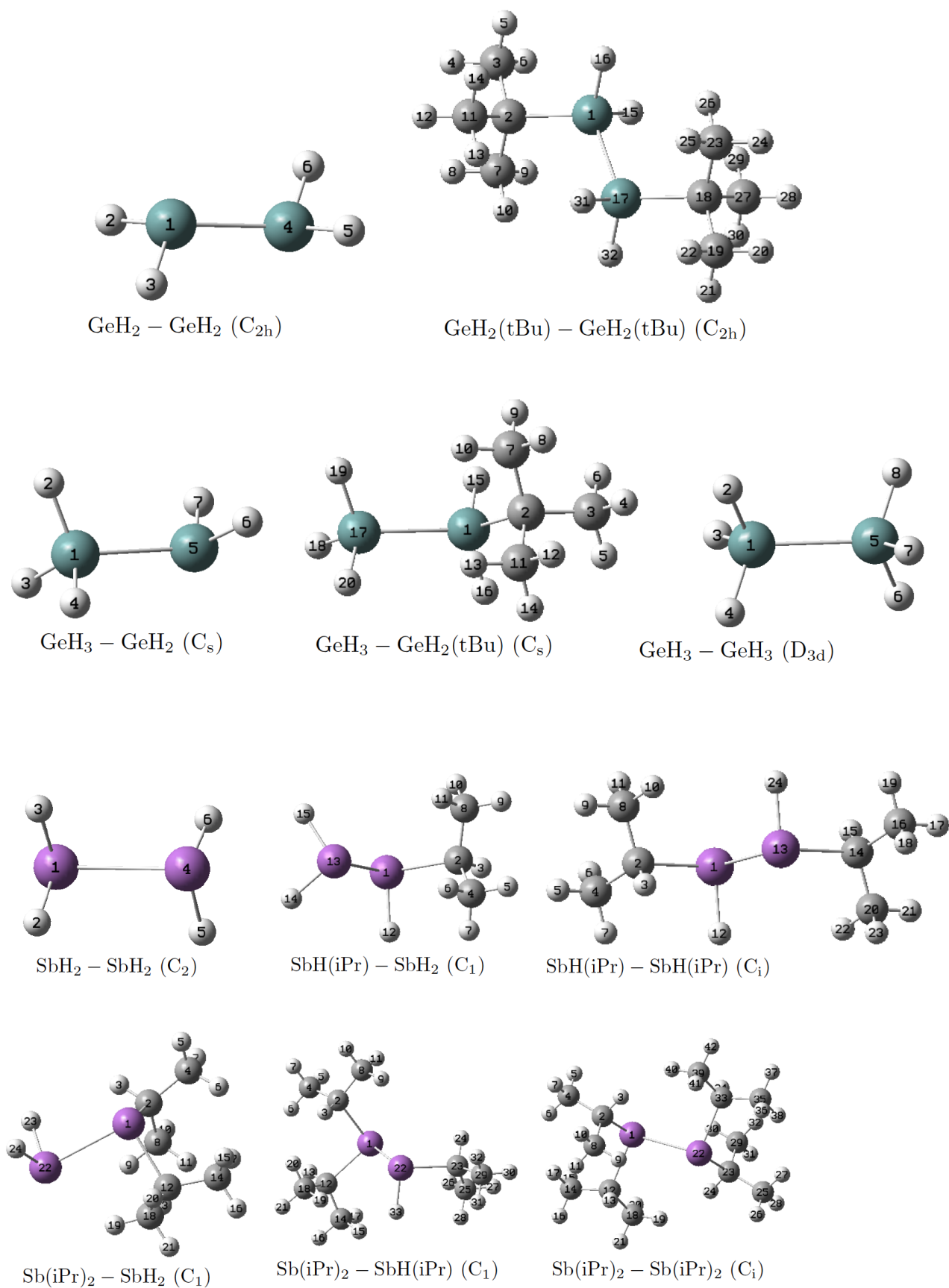
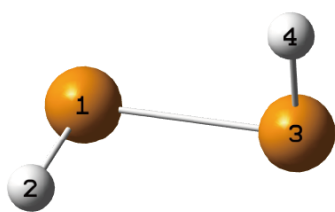
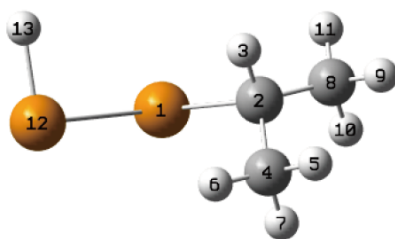


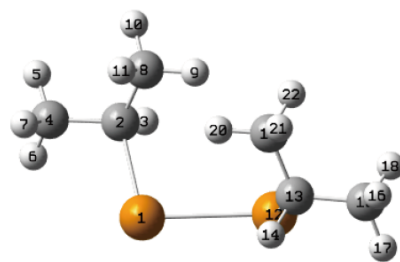
Fig. S10: Optimized structures of the GST molecules we use for our analysis. The molecules with a Ge-Ge bond and those with a Sb-Sb bond are shown.



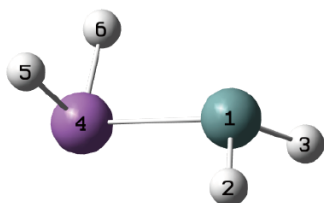
TeH – TeH (C₂)



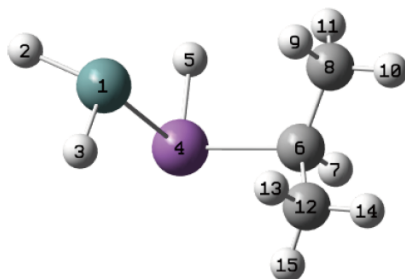
Te(iPr) – TeH (C₁)



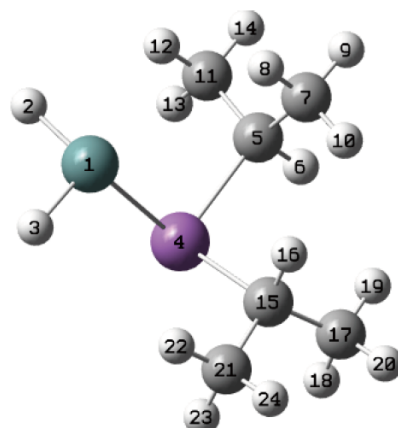
Te(iPr) – Te(iPr) (C₂)



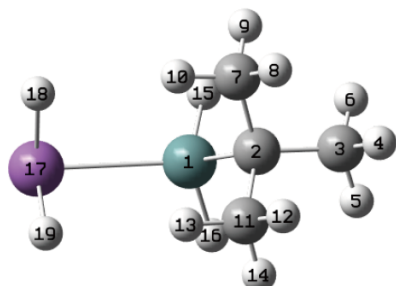
GeH₂ – SbH₂ (C_s)



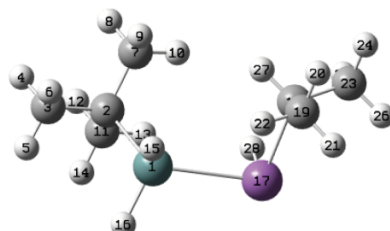
GeH₂ – SbH(iPr) (C₁)



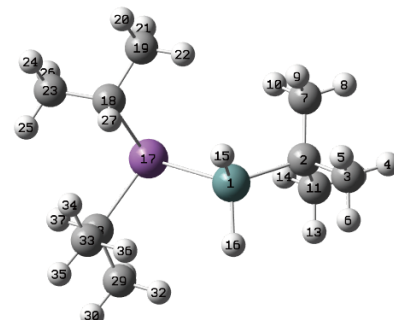
GeH₂ – Sb(iPr)₂ (C₁)



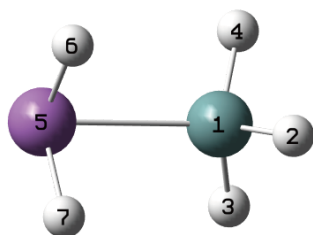
GeH₂(tBu) – SbH₂ (C_s)



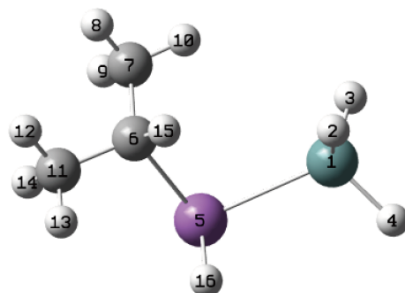
GeH₂(tBu) – SbH(iPr) (C₁)



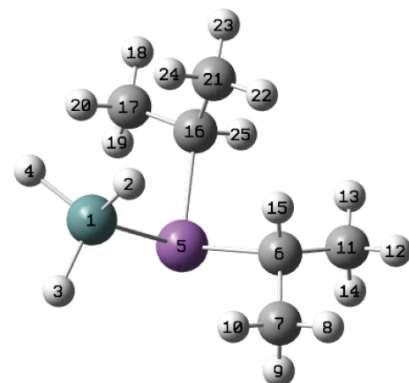
GeH₂(tBu) – Sb(iPr)₂ (C₁)



GeH₃ – SbH₂ (C_s)

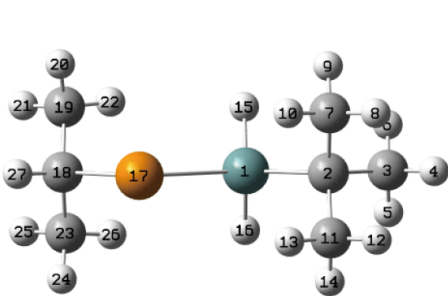


GeH₃ – SbH(iPr) (C₁)

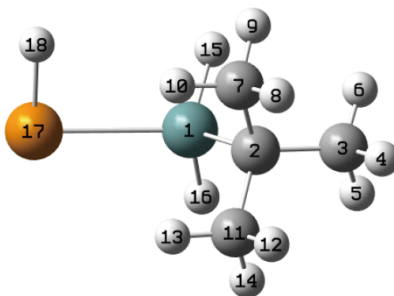


GeH₃ – Sb(iPr)₂ (C₁)

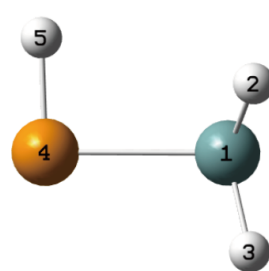
Fig. S1: (*continued*) Optimized structures of the GST molecules we use for our analysis. The molecules with a Te-Te bond and those with a Ge-Sb bond are shown.



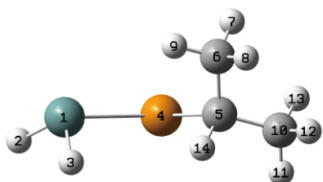
$\text{GeH}_2(\text{tBu}) - \text{Te}(\text{iPr})$ (C_s)



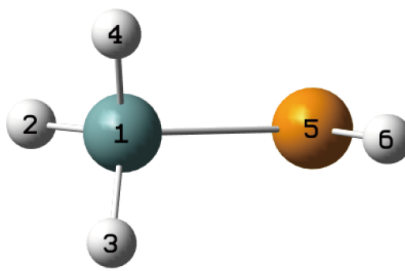
$\text{GeH}_2(\text{tBu}) - \text{TeH}$ (C_1)



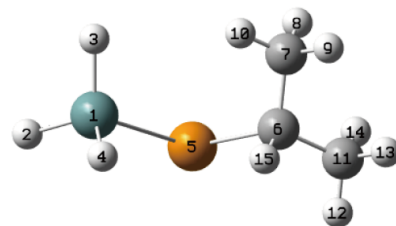
$\text{GeH}_2 - \text{TeH}$ (C_1)



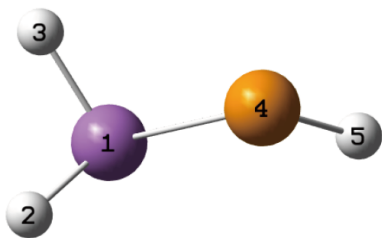
$\text{GeH}_2 - \text{Te}(\text{iPr})$ (C_1)



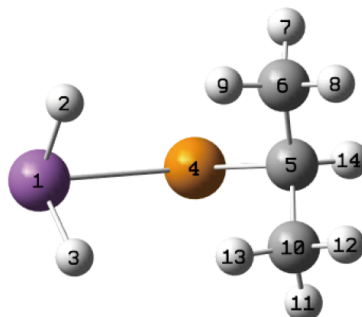
$\text{GeH}_3 - \text{TeH}$ (C_s)



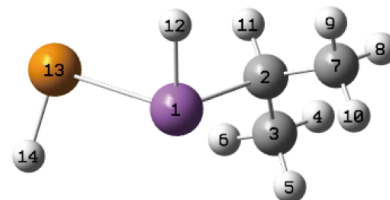
$\text{GeH}_3 - \text{Te}(\text{iPr})$ (C_1)



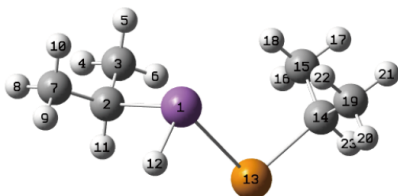
$\text{SbH}_2 - \text{TeH}$ (C_s)



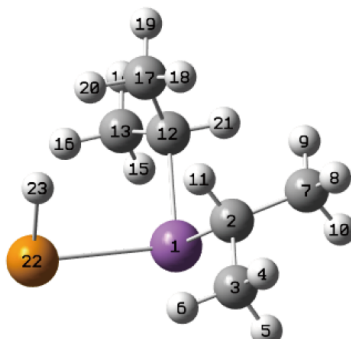
$\text{SbH}_2 - \text{Te}(\text{iPr})$ (C_s)



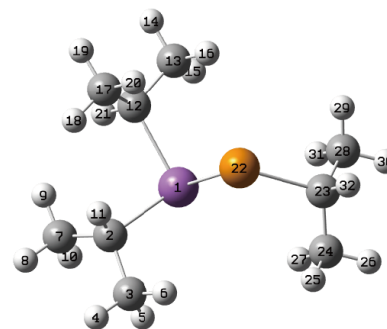
$\text{SbH}(\text{iPr}) - \text{TeH}$ (C_1)



$\text{SbH}(\text{iPr}) - \text{Te}(\text{iPr})$ (C_1)



$\text{Sb}(\text{iPr})_2 - \text{TeH}$ (C_1)



$\text{Sb}(\text{iPr})_2 - \text{Te}(\text{iPr})$ (C_1)

Fig. S1: (*continued*) Optimized structures of the GST molecules we use for our analysis. The molecules with a Ge-Te bond and those with a Sb-Te bond are shown.

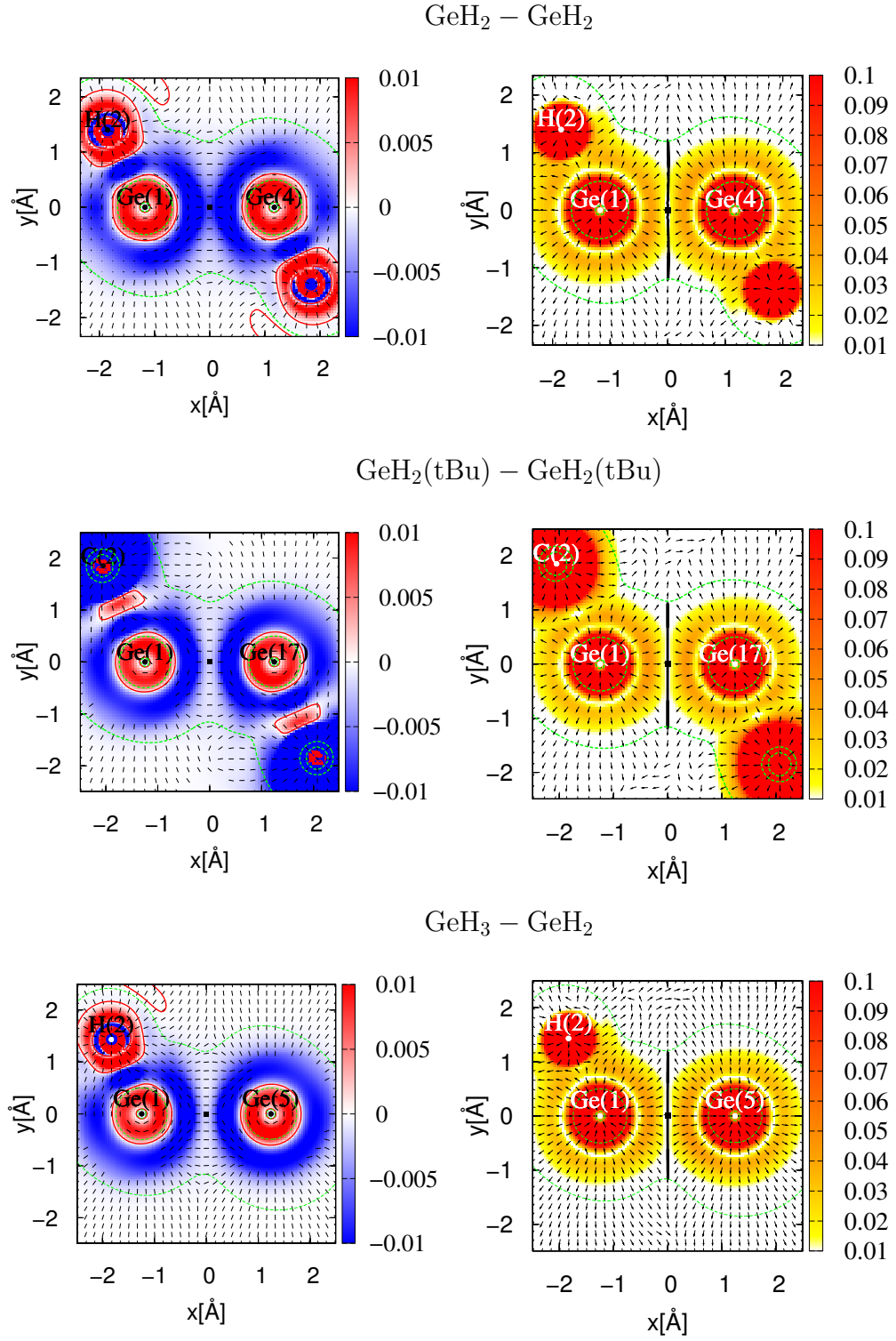


Fig. S2: The largest eigenvalue of the electronic stress tensor density and corresponding eigenvector (left panels), and tension density (right panels), around the GST bonds. The molecules with a Ge-Ge bond are shown.

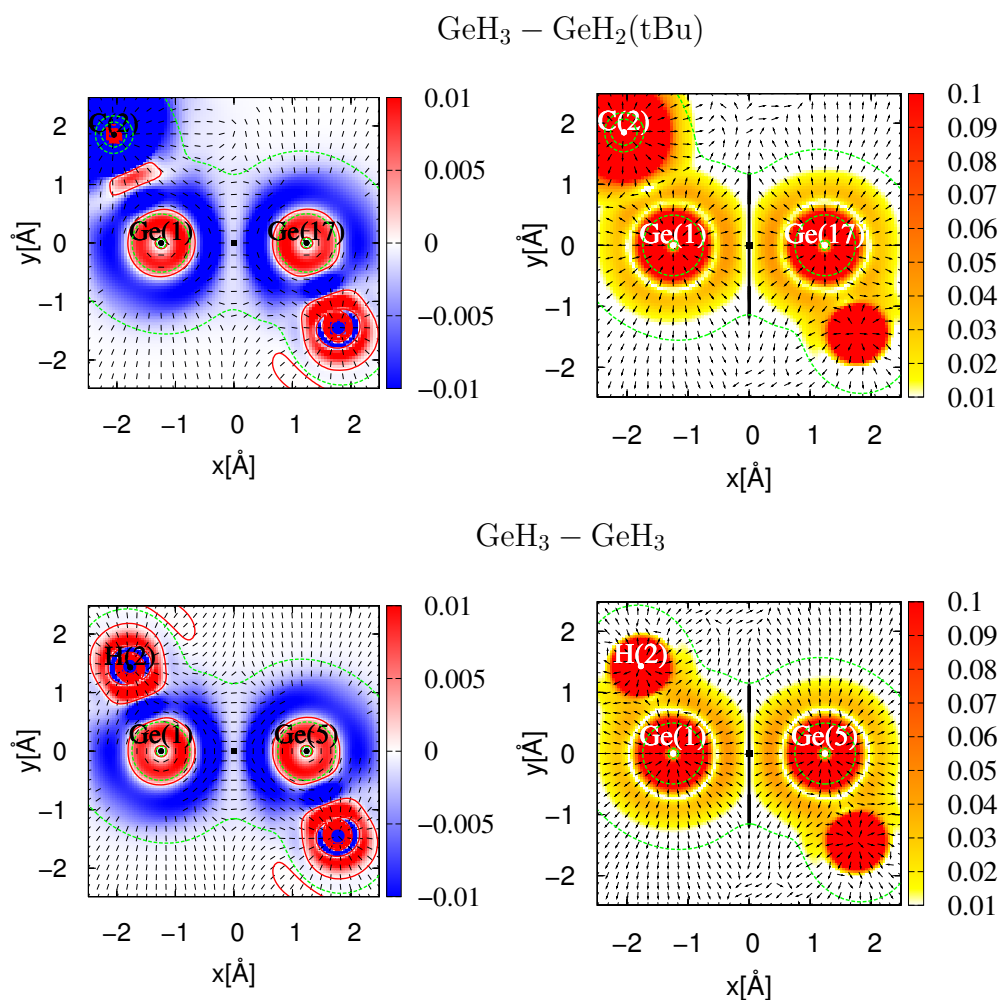


Fig. S2: (*continued*) The largest eigenvalue of the electronic stress tensor density and corresponding eigenvector (left panels), and tension density (right panels), around the GST bonds. The molecules with a Ge-Ge bond are shown.

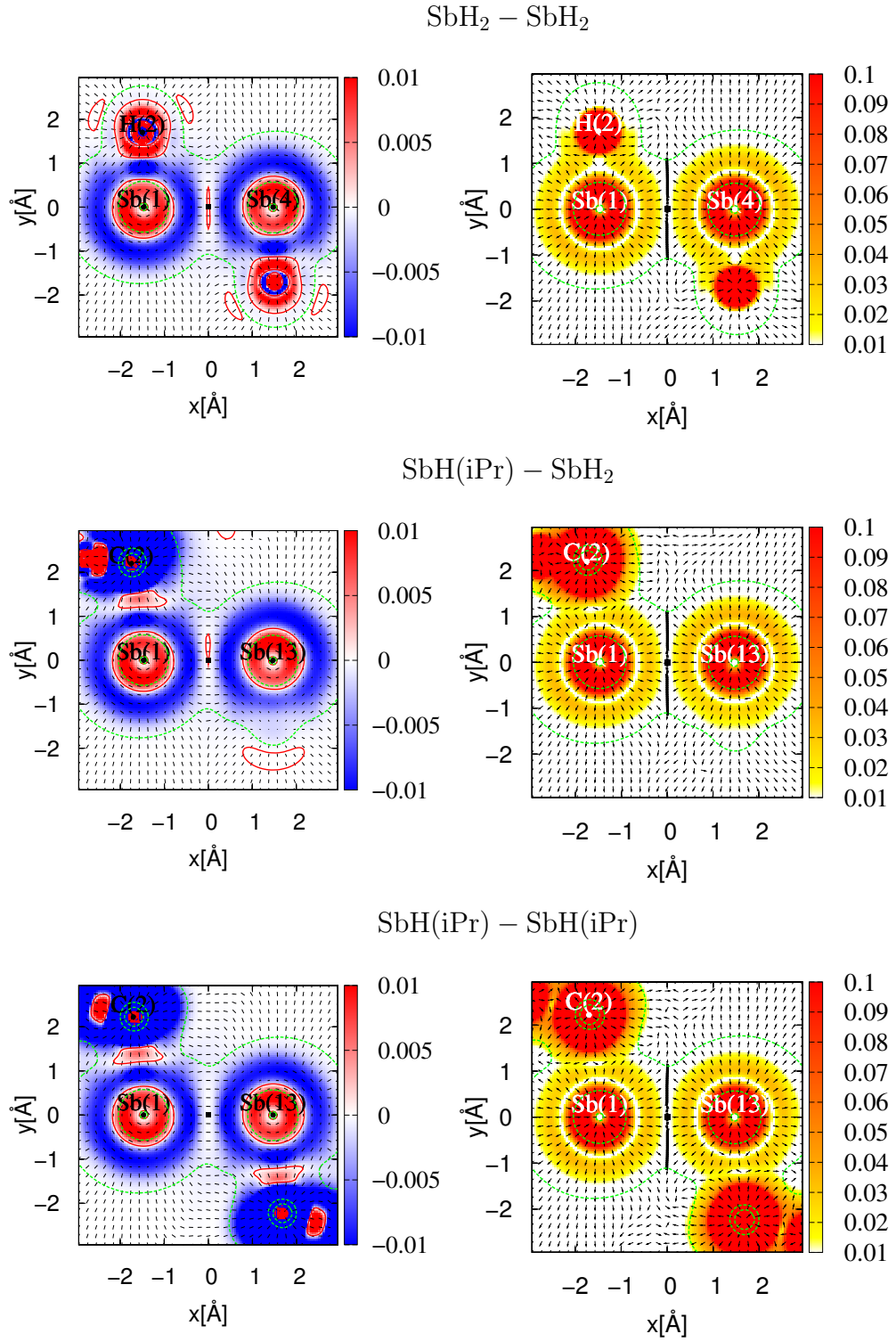


Fig. S2: (*continued*) The largest eigenvalue of the electronic stress tensor density and corresponding eigenvector (left panels), and tension density (right panels), around the GST bonds. The molecules with a Sb-Sb bond are shown.

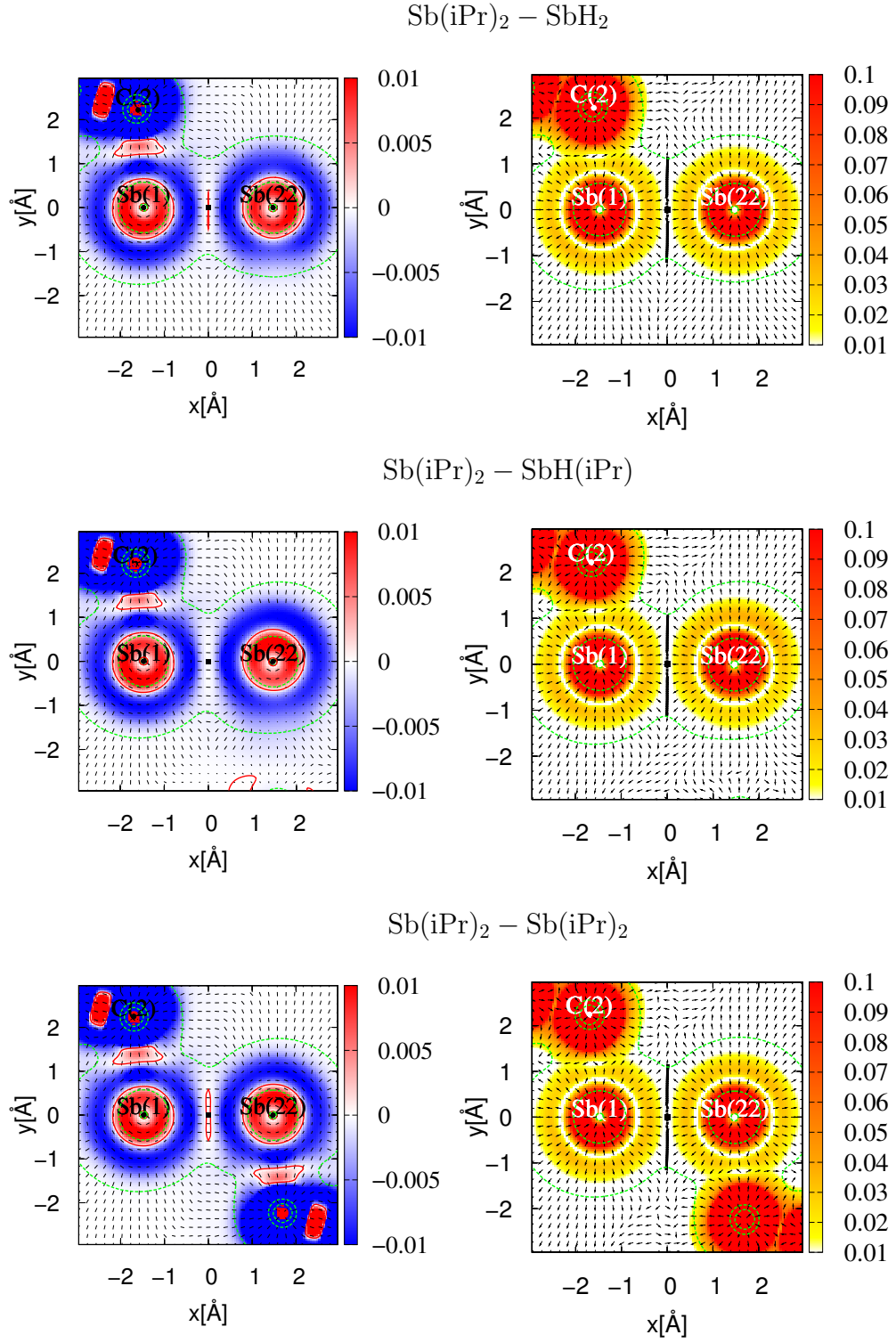


Fig. S2: (*continued*) The largest eigenvalue of the electronic stress tensor density and corresponding eigenvector (left panels), and tension density (right panels), around the GST bonds. The molecules with a Sb-Sb bond are shown.

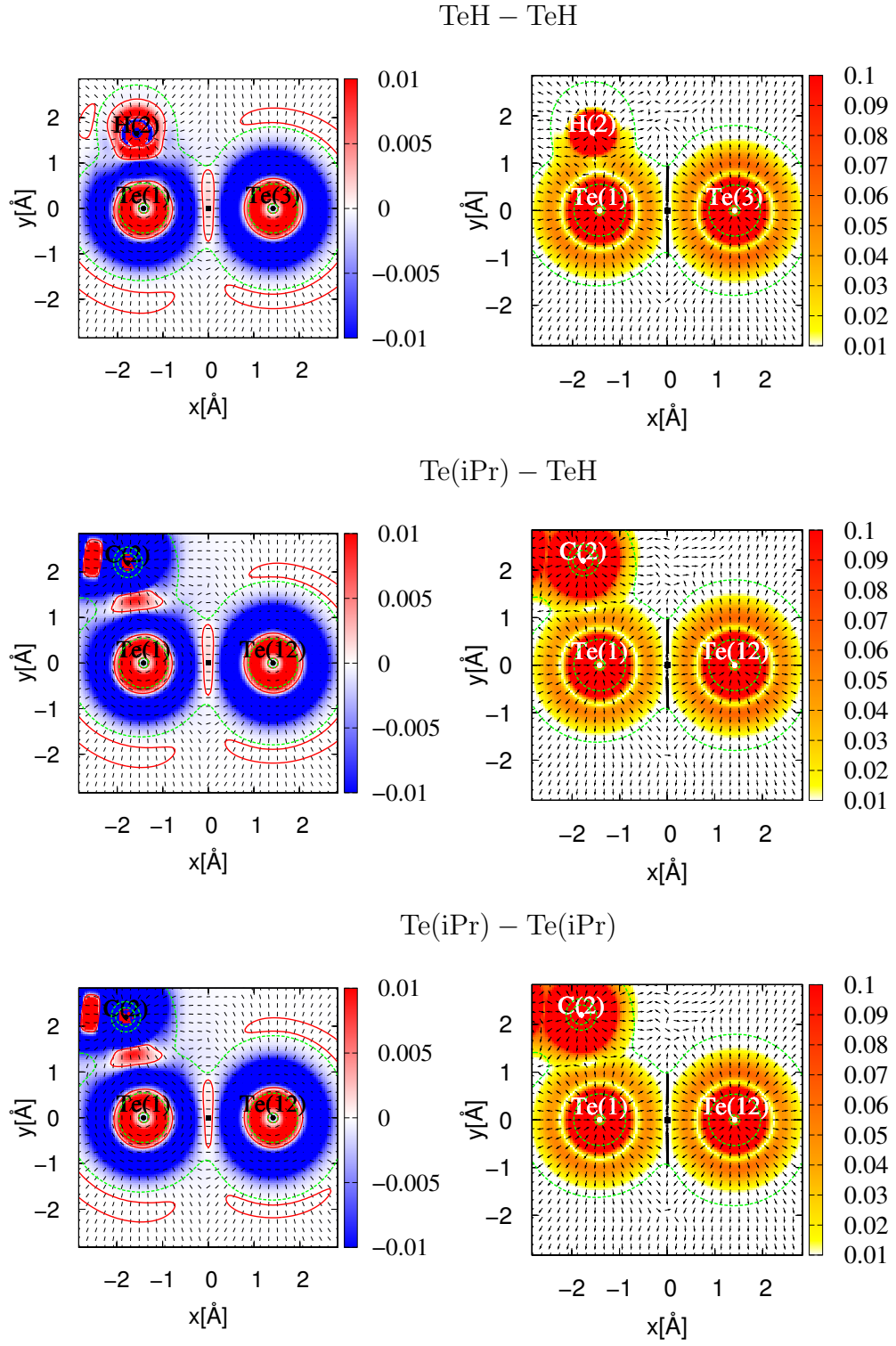


Fig. S2: (*continued*) The largest eigenvalue of the electronic stress tensor density and corresponding eigenvector (left panels), and tension density (right panels), around the GST bonds. The molecules with a Te-Te bond are shown.

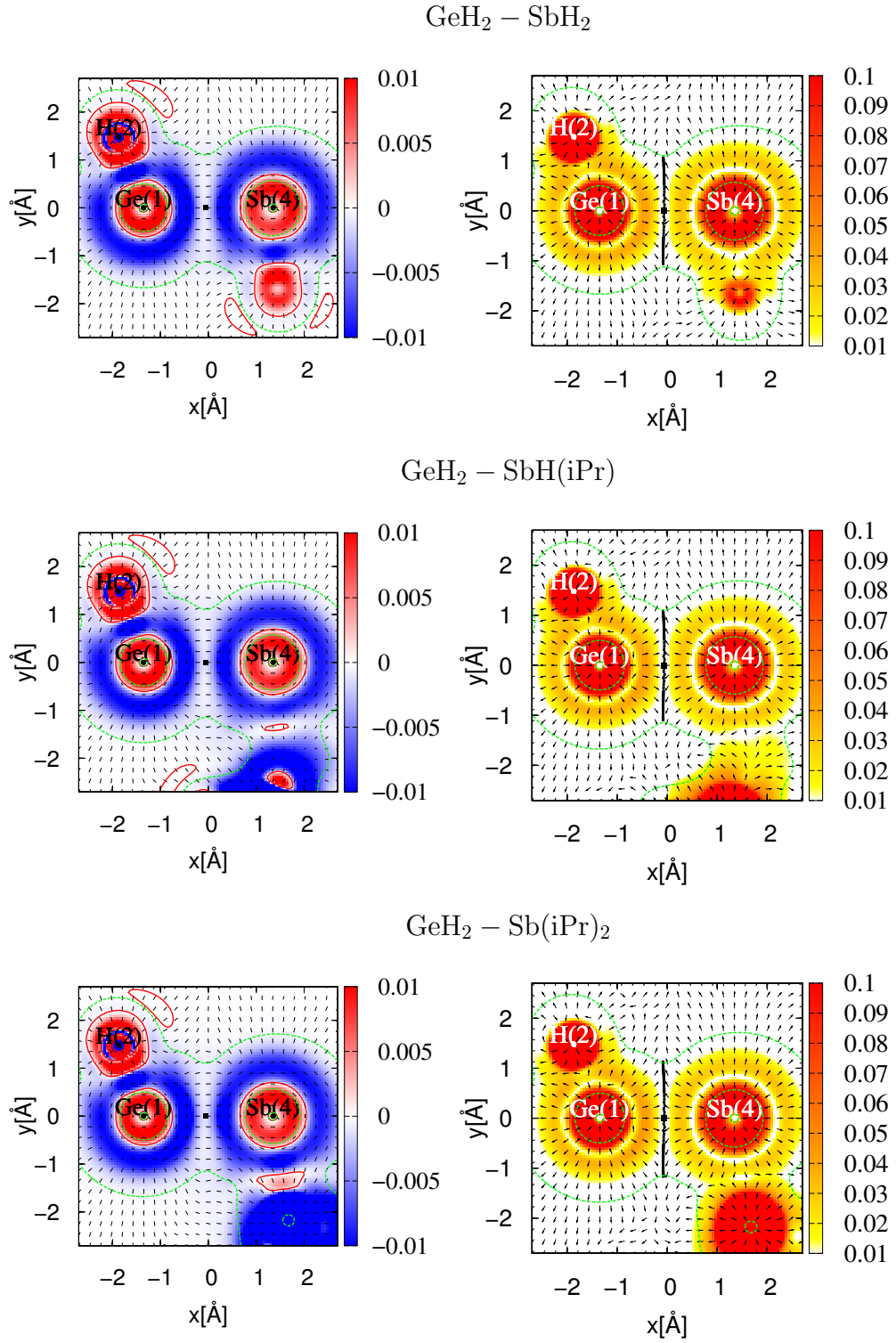


Fig. S2: (*continued*) The largest eigenvalue of the electronic stress tensor density and corresponding eigenvector (left panels), and tension density (right panels), around the GST bonds. The molecules with a Ge-Sb bond are shown.

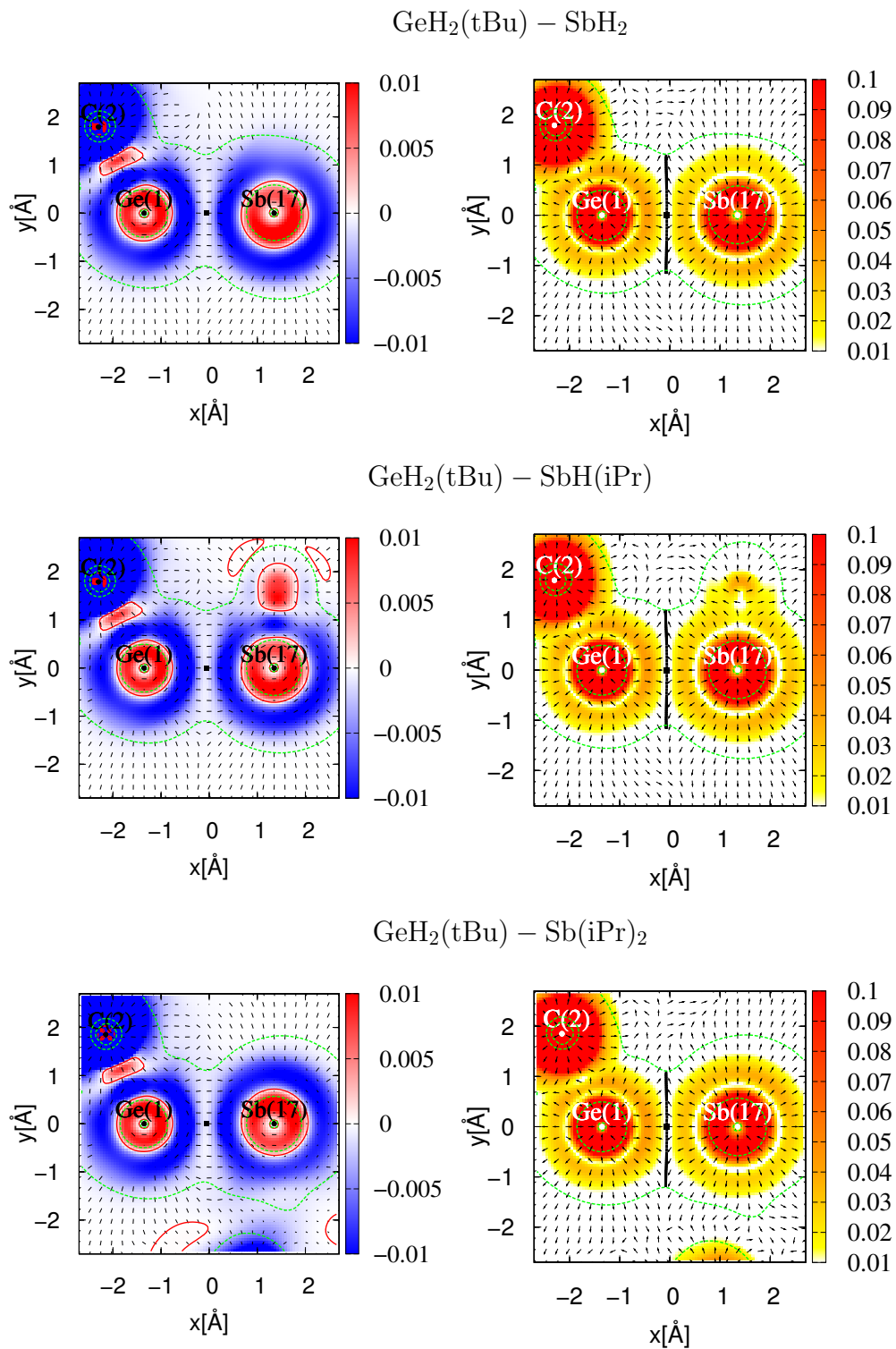


Fig. S2: (*continued*) The largest eigenvalue of the electronic stress tensor density and corresponding eigenvector (left panels), and tension density (right panels), around the GST bonds. The molecules with a Ge-Sb bond are shown.

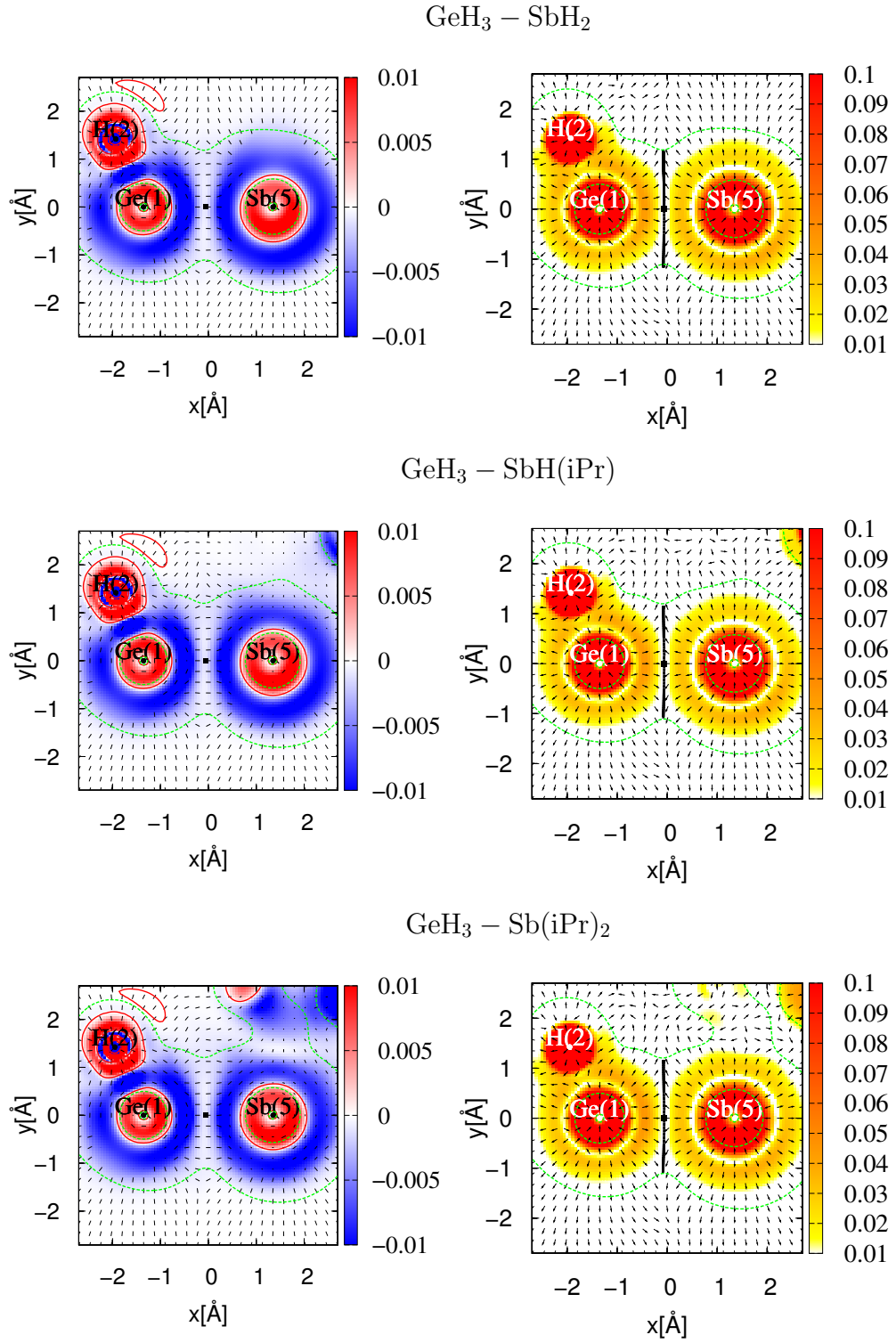


Fig. S2: (*continued*) The largest eigenvalue of the electronic stress tensor density and corresponding eigenvector (left panels), and tension density (right panels), around the GST bonds. The molecules with a Ge-Sb bond are shown.

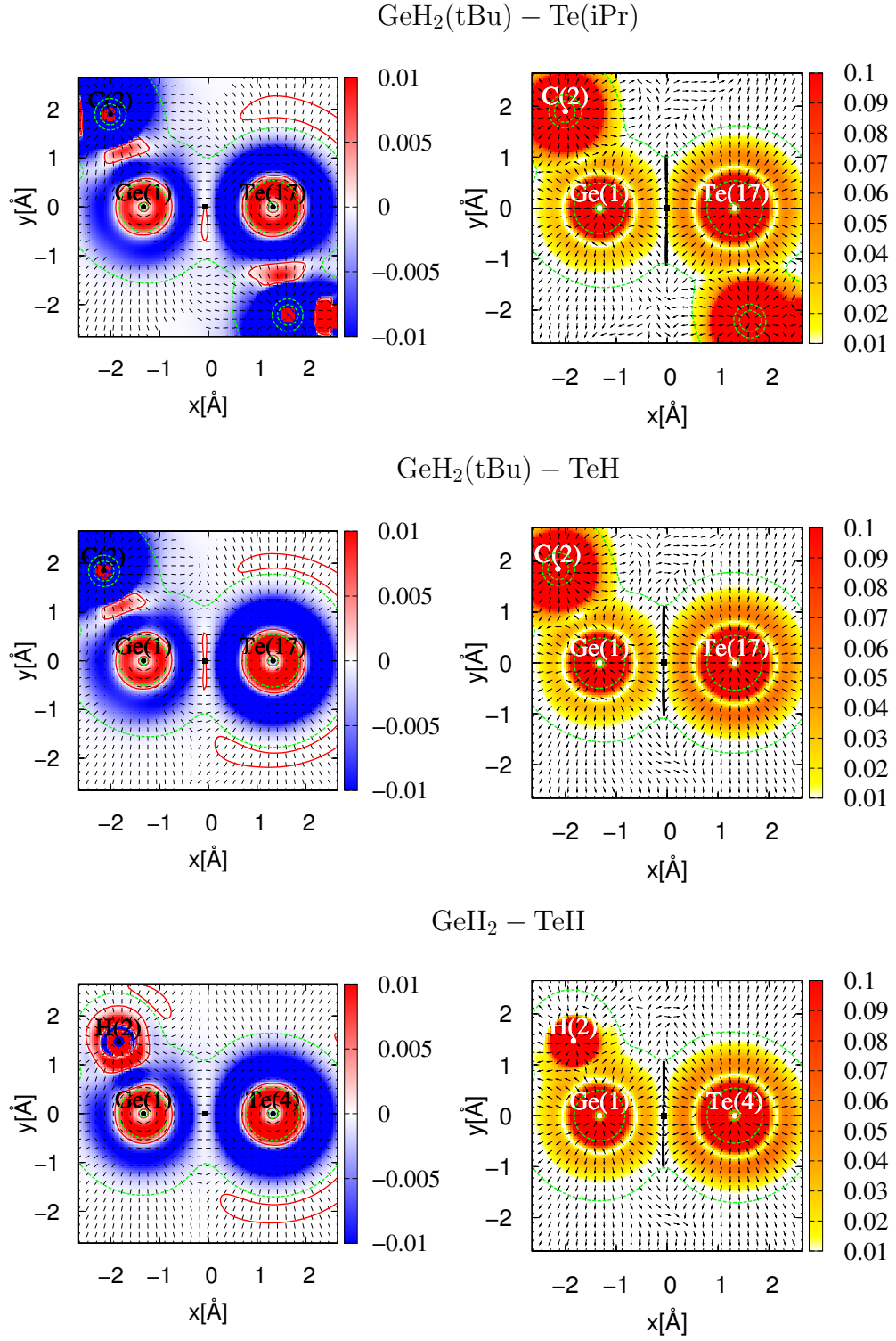


Fig. S2: (*continued*) The largest eigenvalue of the electronic stress tensor density and corresponding eigenvector (left panels), and tension density (right panels), around the GST bonds. The molecules with a Ge-Te bond are shown.

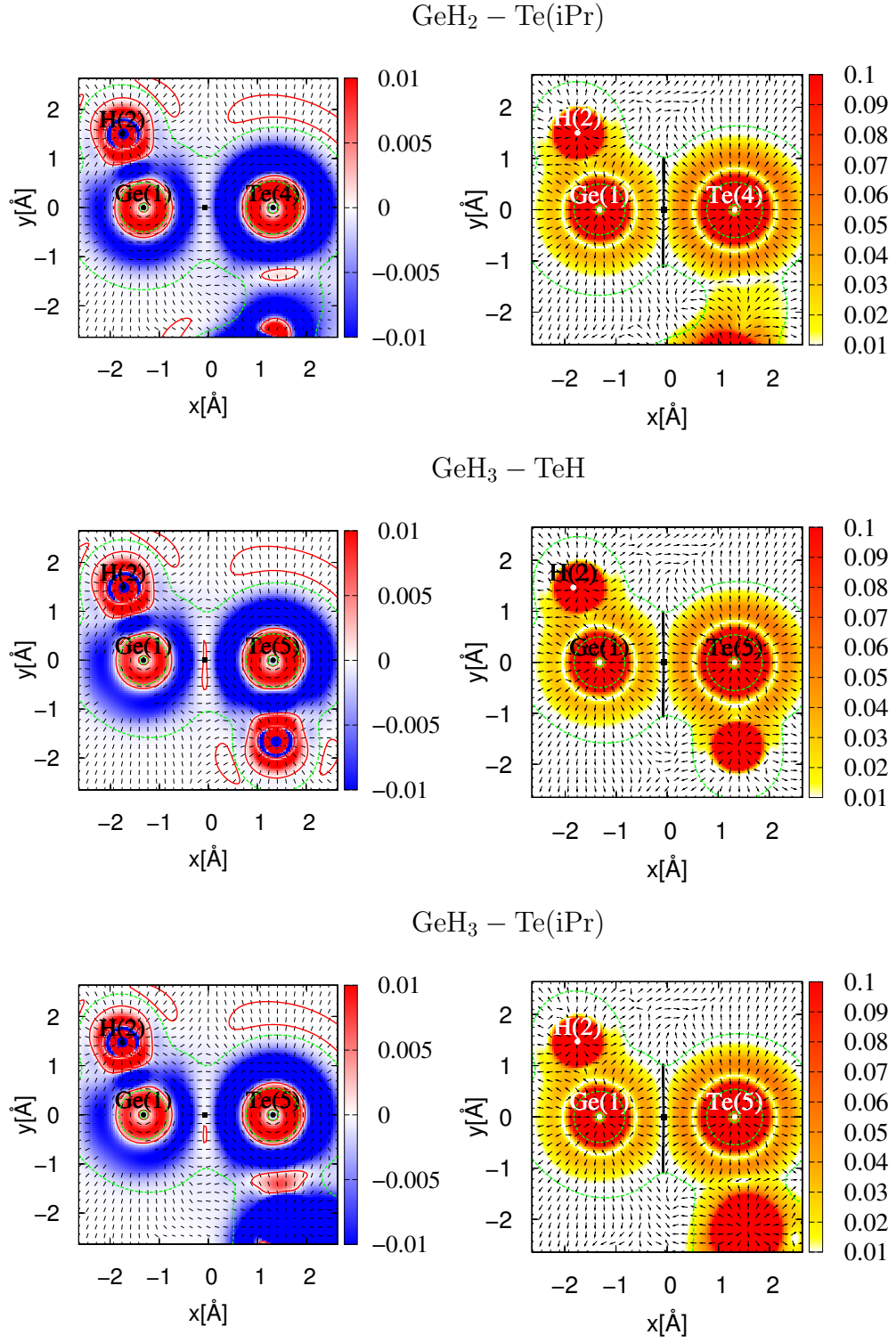


Fig. S2: (*continued*) The largest eigenvalue of the electronic stress tensor density and corresponding eigenvector (left panels), and tension density (right panels), around the GST bonds. The molecules with a Ge-Te bond are shown.

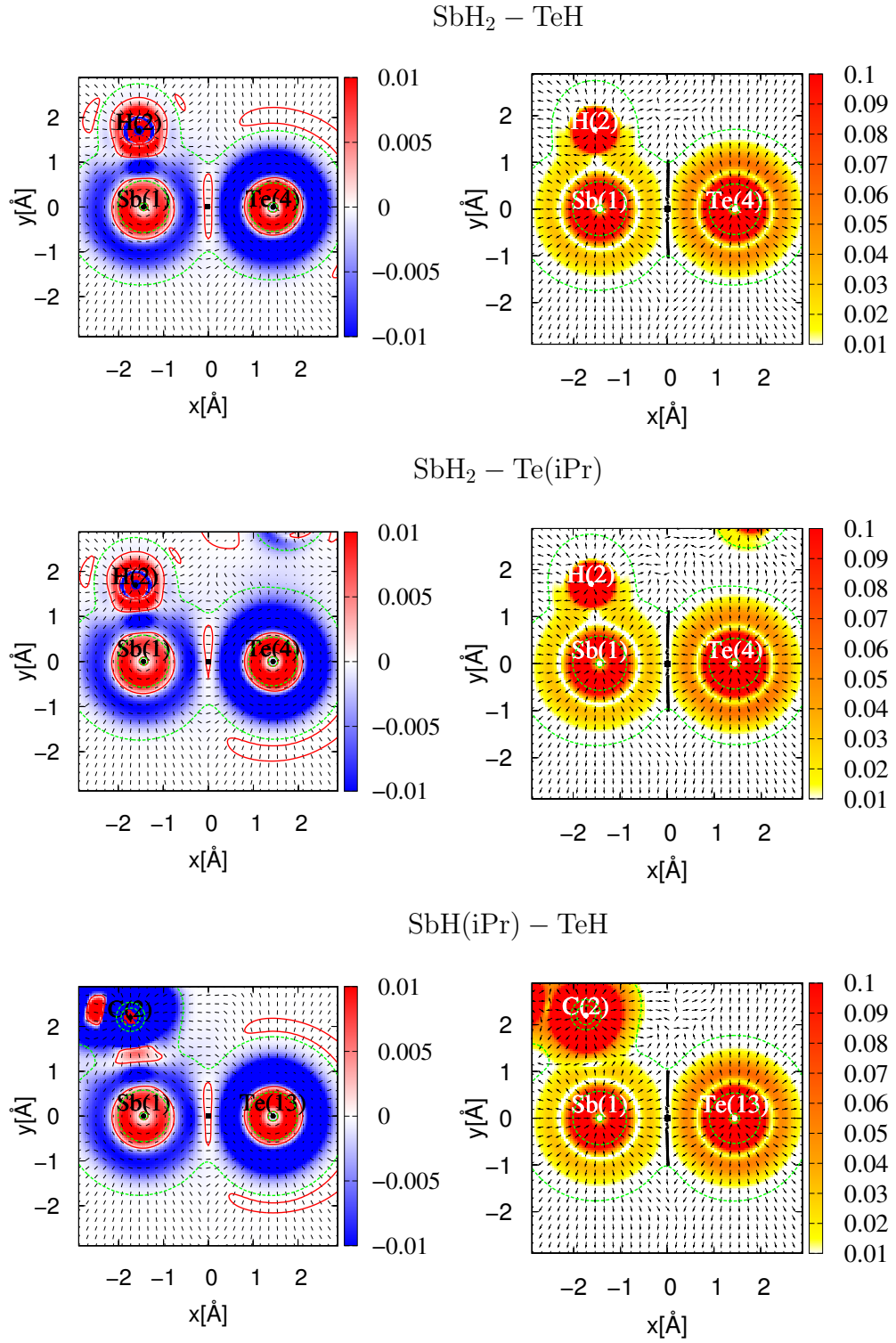


Fig. S2: (*continued*) The largest eigenvalue of the electronic stress tensor density and corresponding eigenvector (left panels), and tension density (right panels), around the GST bonds. The molecules with a Sb-Te bond are shown.

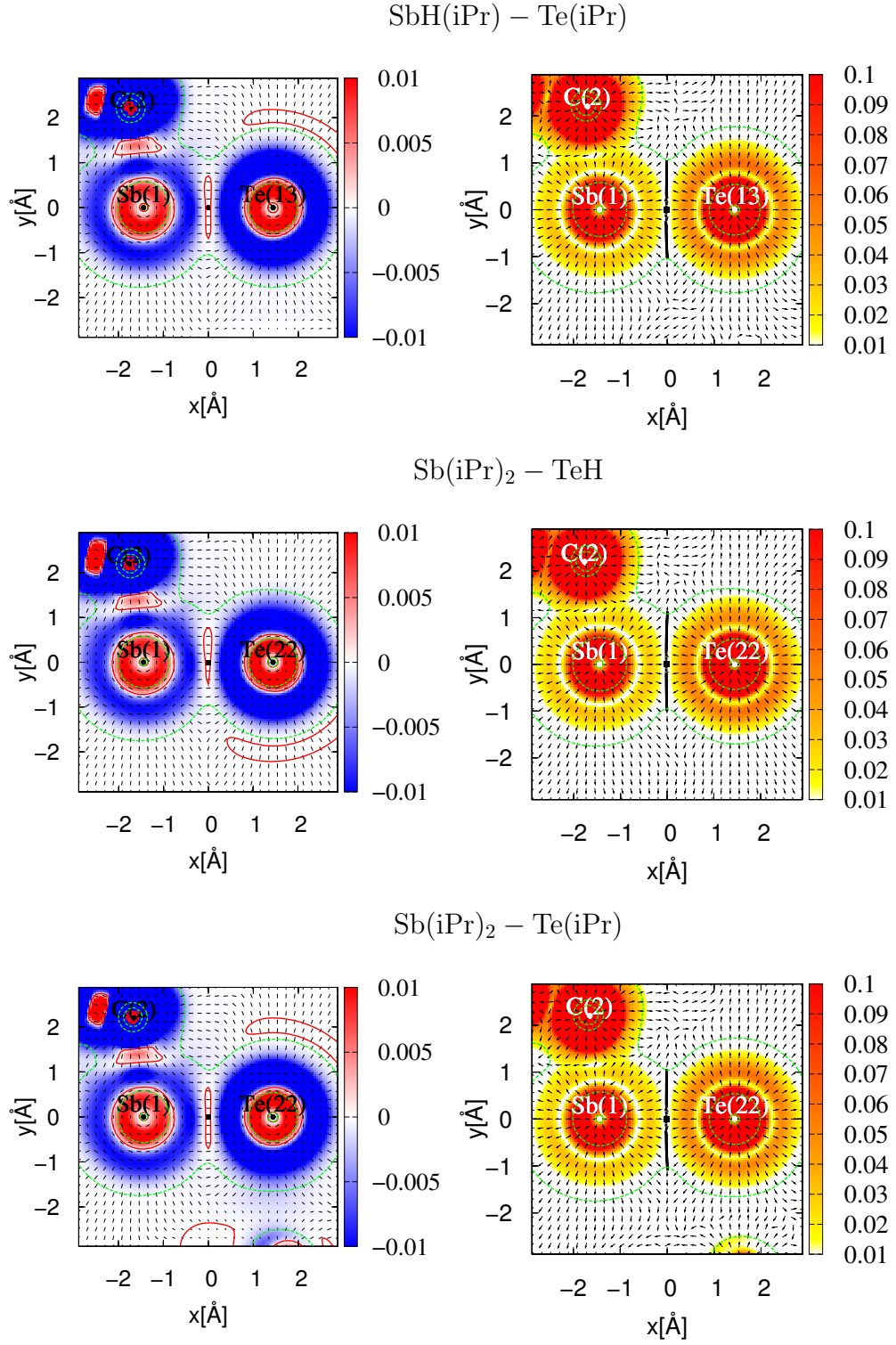


Fig. S2: (*continued*) The largest eigenvalue of the electronic stress tensor density and corresponding eigenvector (left panels), and tension density (right panels), around the GST bonds. The molecules with a Sb-Te bond are shown.

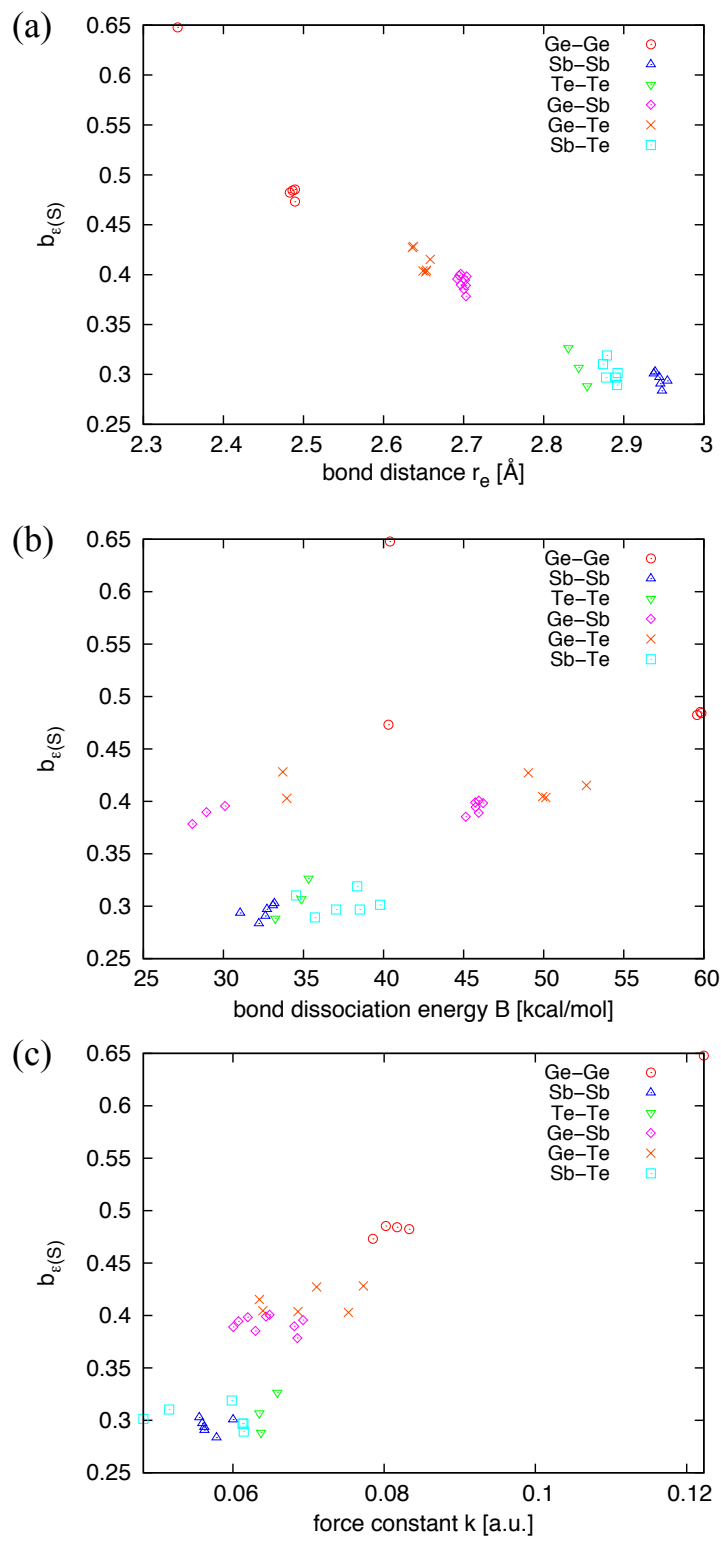


Fig. S3: The relation between energy density based bond order $b_{\epsilon(S)}$ and (a) bond distance, (b) dissociation energy, and (c) force constant, for the GST bonds. The correlation coefficients are -0.970 , 0.569 , and 0.887 , respectively.

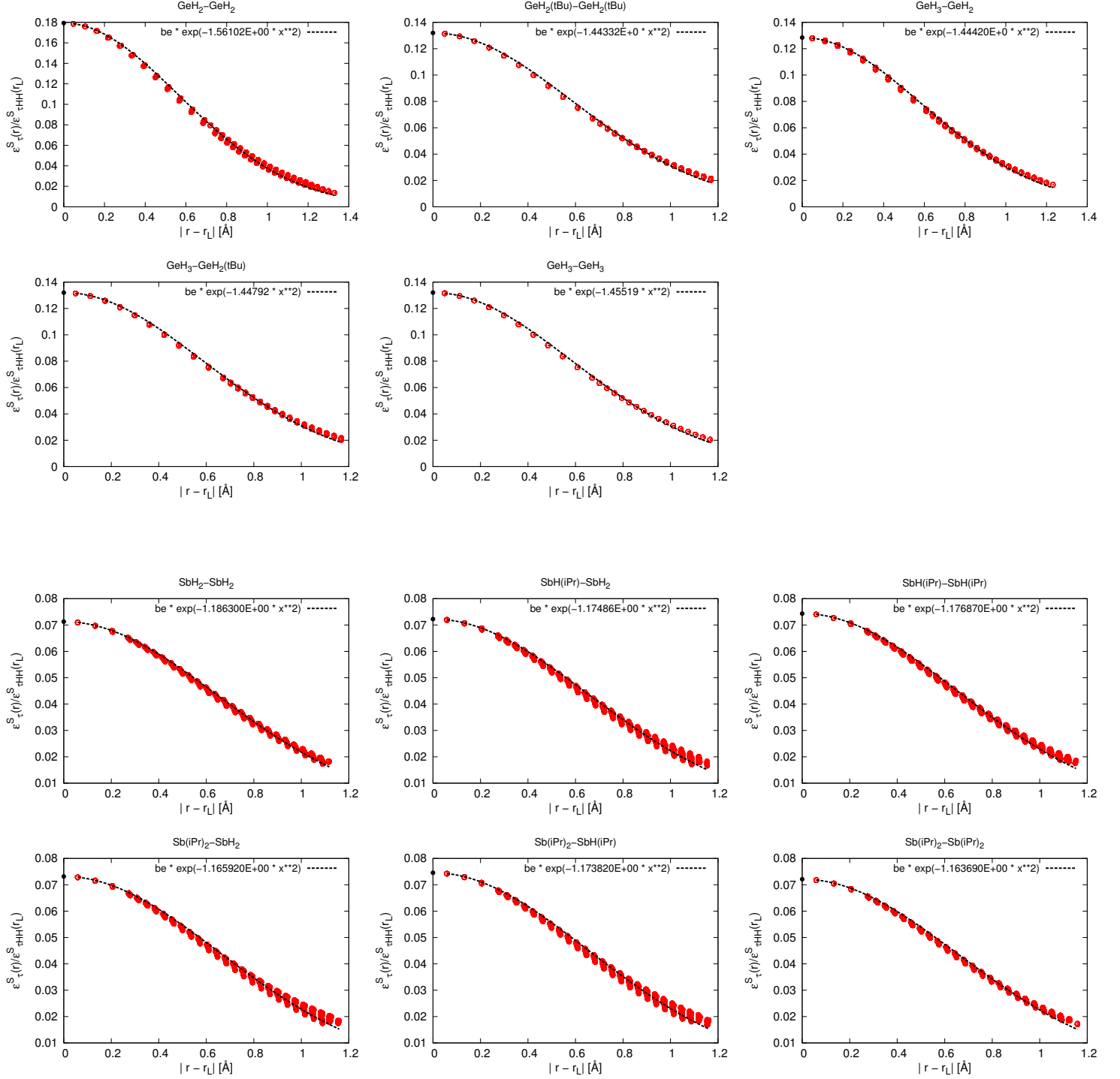


Fig. S4: The energy density distribution and fitting Gaussian functions on the Lagrange surface between the Ge-Ge bonds and Sb-Sb bonds.

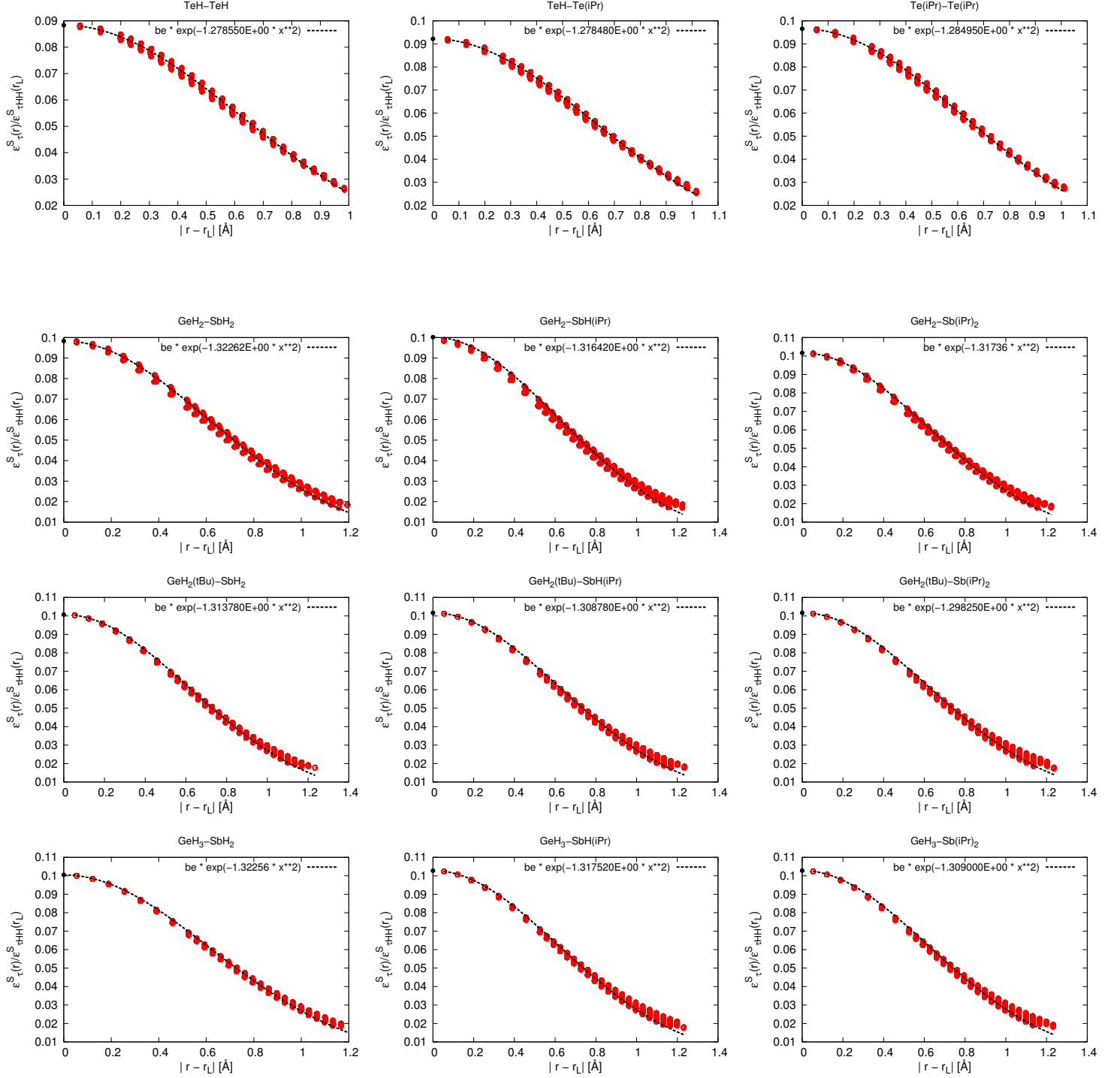


Fig. S4: (*continued*) The energy density distribution and fitting Gaussian functions on the Lagrange surface between the Te-Te bonds and Ge-Sb bonds.

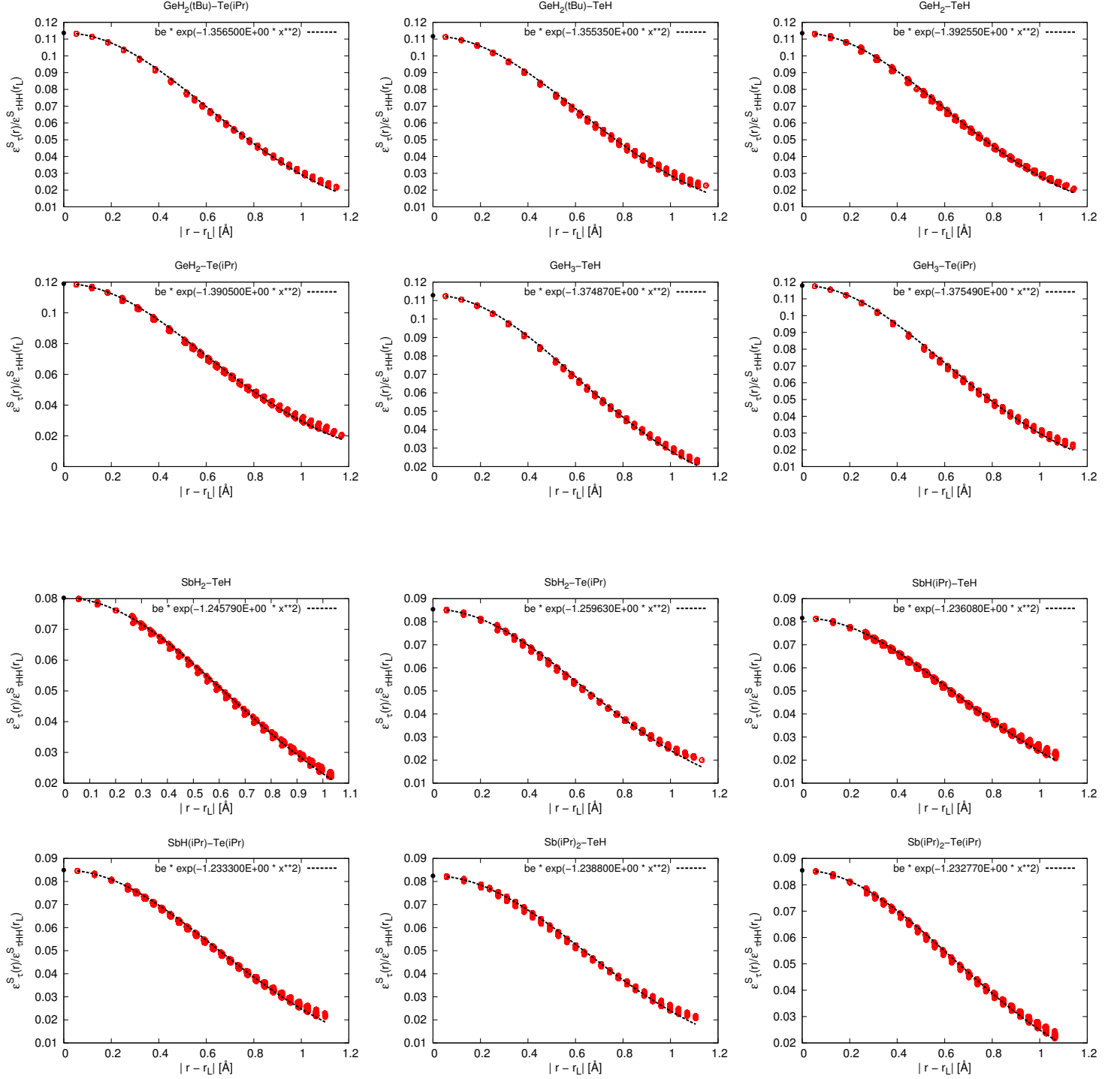


Fig. S4: (*continued*) The energy density distribution and fitting Gaussian functions on the Lagrange surface between the Ge-Te bonds and Sb-Te bonds.

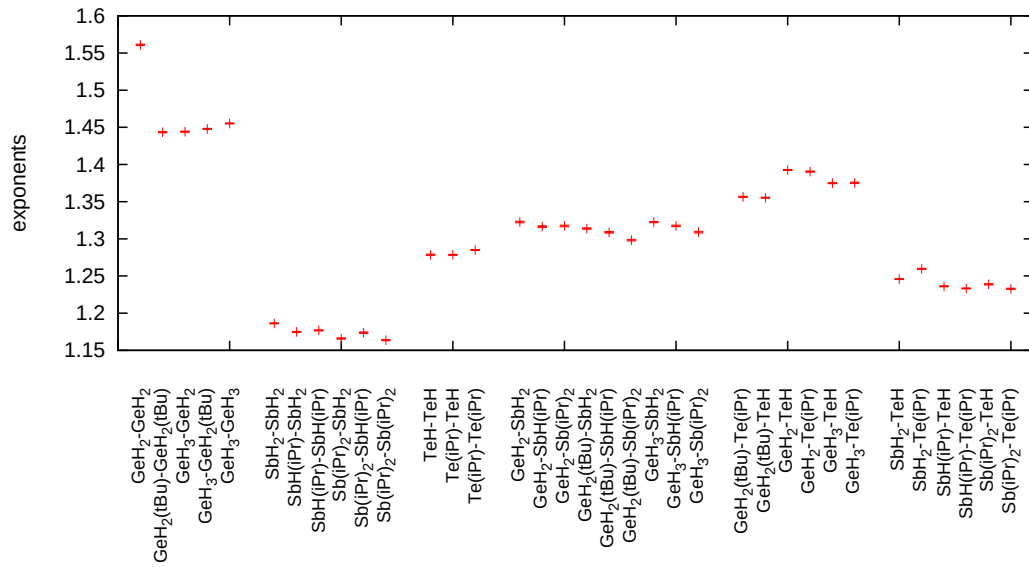


Fig. S5: Summary of the fitting parameter α for the energy density distribution on the Lagrange surface between the GST bonds.

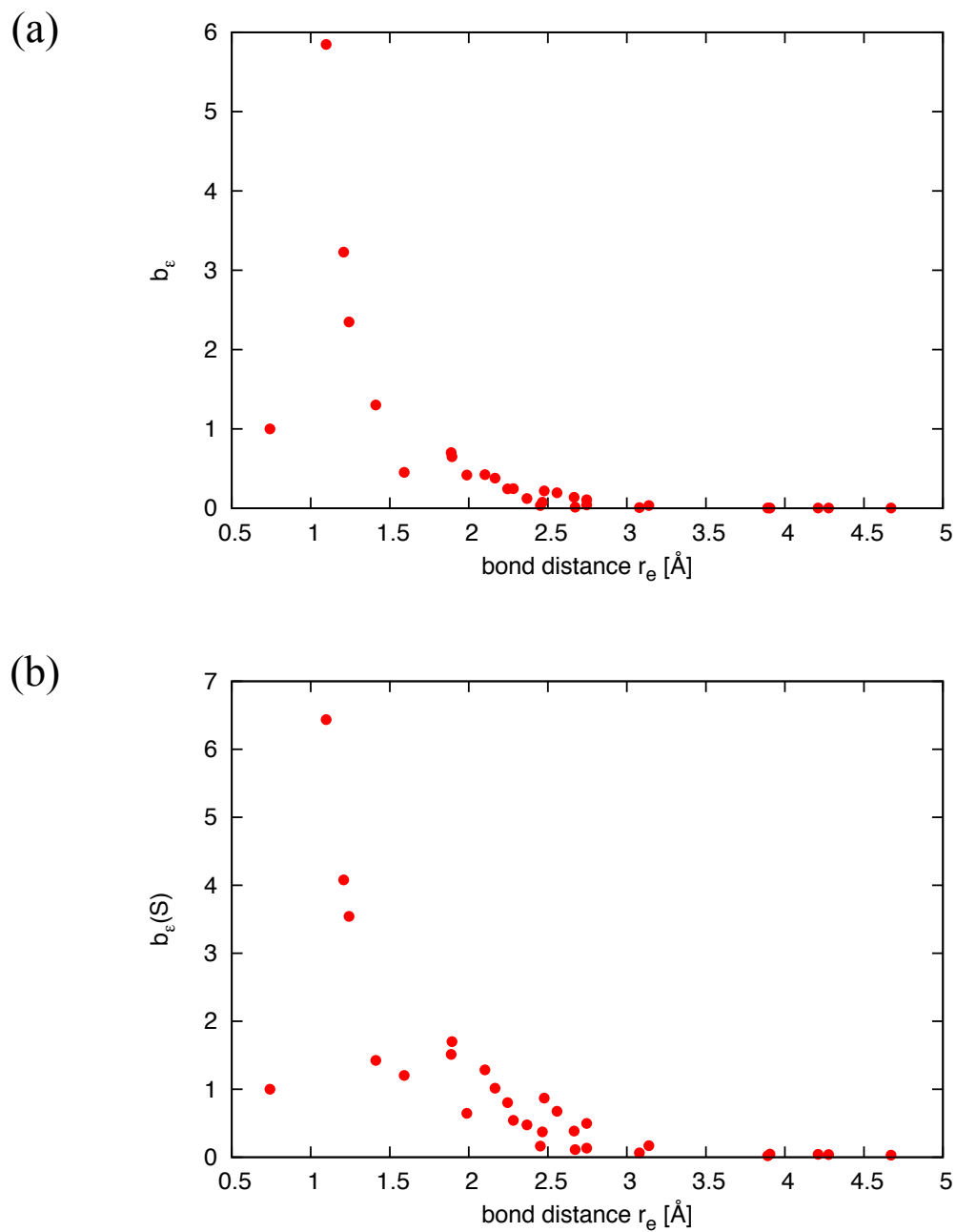


Fig. S6: The relation between bond distance r_e and (a) b_ϵ and (b) $b_{\epsilon(S)}$, for the bonds in the homonuclear diatomic molecules. The correlation coefficients are -0.583 and -0.651 respectively.

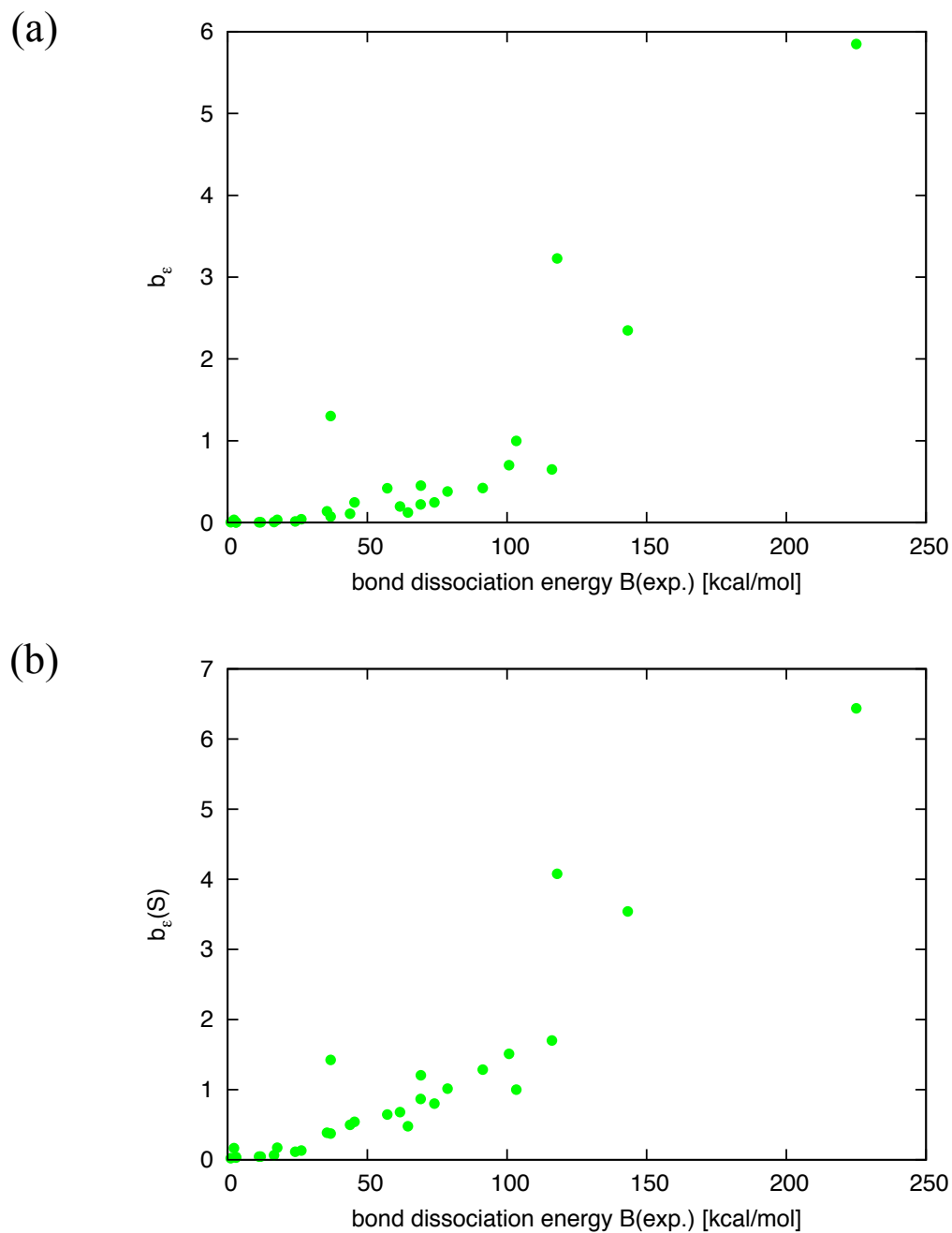


Fig. S7: The relation between bond dissociation energy B and (a) b_ϵ and (b) $b_{\epsilon(S)}$, for the bonds in the homonuclear diatomic molecules. The correlation coefficients are 0.834 and 0.906 respectively.

Chapter 5

5 Bonding in Doped Gallium Nanoclusters: Insights from Regional DFT

5.1 Introduction

The high surface-to-bulk ratio of cluster-based materials provides new and unique surfaces for exploring chemical reactivity [1–4]. Although these materials have significant potential for catalysis and novel applications, the investigations of these materials for these purposes is often ad hoc rather than systematic. However, a detailed understanding of the bonding in clusters can be used to identify features that will facilitate manipulation of cluster properties for specific applications.

In bulk gallium metal, each atom has one very close neighbour at $\sim 2.44\text{\AA}$, while the other neighbours are found at $2.70 \sim 2.79\text{\AA}$ [5]. In this context, the shorter interactions might be considered as diatomic subunits (Ga_2) and bulk gallium might almost be considered a molecule material. Formation of Ga_2 subunits is also observed in the structure of many small clusters [6]. The molecular $(\text{Ga}_2)_n$ nature of bulk α -gallium has been proposed as an explanation for its low melting temperature (30°C). Small particles of gallium are expected to have even lower melting temperatures due to the change in surface to volume ratio and the impact this has on cohesive energy [7]. In fact for particles composed of thousands of atoms the decrease in melting temperature is linked to particle radius [8]. However, experimental studies have revealed that many gallium clusters (> 500 atoms) exhibit melting temperatures substantially higher than the bulk [9–12]. Chacko et al. proposed that covalent bonding in small clusters explains the higher melting temperature of these species [13]. In contrast to this, separate studies by Núñez et al. [14] and Steenbergen and Gaston [15] suggest that these clusters have metallic or free-electron-like bonding. As Pyfer et al. note, the finite temperature behaviour of these clusters is directly linked to the geometry and bonding in the ground state [12]. Steenbergen and Gaston have explored this in some detail and have been able to link cluster structures to gallium bulk phases and the corresponding electronic states. This approach has provided insight to the size dependence of the electronic structure and the melting behaviour.

The electronic ground state of the Ga_2 molecule is $^3\Pi_u$ [16] with an experimental bond length of $2.75\text{\AA}$ [17]. The Ga_2 molecule formally has a bond order of 1, with the $2\sigma_g^+$ and one of the π_u orbitals singly occupied (Fig. 1). The single bond between the gallium atoms is formally covalent but clearly has both σ and π character. The long bond length of this electronic state arises largely from the σ overlap requirements of the $4p_x$ orbitals that form the $2\sigma_g^+$ molecular orbital. Tonner and Gaston also note that in the $^3\Sigma_g^-$ excited triplet state, the $2\sigma_g^+$ orbital is empty and now both of the π_u -orbitals are singly occupied. This leads to a formal bond order of one with only π -character but the electrons are more delocalized than in a typical π -bond [18].

Tonner and Gaston also recently investigated a number of small clusters and compared these with the structure of α -gallium [13]. Their density functional calculations clearly identify Ga_2 subunits as building blocks in Ga_4 and Ga_8 clusters. However, for Ga_6 the molecular orbitals appear to be built from a combination of Ga_2 and atomic orbitals, which highlights the complex nature of bonding in these species. Using Atoms in Molecules (AIM) analysis, they were able to show that the short interatomic distance in bulk α -gallium can be related to the $^3\Sigma_g^-$ state of Ga_2 .

Although $(\text{Ga}_2)_n$ character of small clusters declines beyond Ga_8 , it is noticeable that Ga_2 subunits are evident in the equatorial region of Ga_{12}X clusters. However, as shown previously [19] the Ga_2 subunits and axial bonds of these clusters are particularly sensitive to changes in the bonding environment within the cluster. In our recent study [20] we probed the reactivity of doped gallium nanoclusters and identified distinct regioselectivity for hydrogen adsorption. In particular, adsorption sites could be

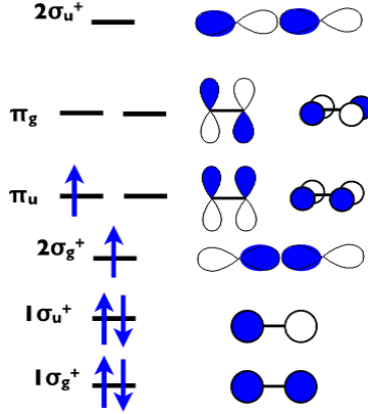


Fig. 1: Qualitative molecular orbitals of Ga_2 in the $^3\Pi_u$ ground state.

linked to the dopant and valence electronic configuration. In the pure Ga_{13} cluster, hydrogen adsorption occurs at or adjacent to the Ga_2 subunits. However, addition of dopants (Si, P, Ge or As) that increase the total number of valence electrons in the cluster leads to changes in the preferred adsorption sites. In particular, there is increased reactivity at the axial positions and decreased reactivity at hollow sites. Clusters with n-type dopants have a closed 1F shell within the Jellium model and in the case of Ga_{12}P and Ga_{12}As , there is opening of the next electronic shell. This leads to more localized covalent bonding with hydrogen. In comparison, clusters with group 13 dopants have a partially filled 1F shell and generally exhibit delocalized bonding to hydrogen.

Previously [21,22] we have found that Regional Density Functional Theory (RDFT) analysis provides significant information regarding the bonding and reactivity of nanocluster species. The RDFT method revealed differences between the bonding inside aluminium cluster cages and those of the surface bonds that correlated with observed regioselectivity in reactions of the clusters. For example, metallic bonds generally hinder H_2 adsorption, whereas more covalent bonds favour H_2 .

The Regional DFT [23] and electronic stress tensor method were applied in this study to investigate the bonding in Ga_2 and Ga_{12}X clusters ($\text{X} = \text{B}, \text{C}, \text{N}, \text{Al}, \text{Si}, \text{P}, \text{Ga}, \text{Ge}$ or As) and to explain trends in hydrogen adsorption as a function of dopants.

5.2 Theoretical Procedures

The analysis carried out in this study was performed on the lowest energy endohedral (endo- Ga_{12}X) and exohedral (exo- XGa_{12}) isomers identified previously [14] at the PBE0/6-311G(d,p) level using the GAUSSIAN09 [24] computer program. Electronic stress tensor and energy density calculations were performed with the QEDynamics program package [25] using the relevant electronic wavefunctions obtained from the PBE0/6-311G(d,p) structures. Electron deformation densities were obtained from PBE/DNP geometries using DMOL³ [26, 27]. All structures were confirmed as true minima using vibrational frequency analysis.

The RDFT and electronic stress tensor method have previously been reported in detail [28–31]. The zero kinetic energy isosurface was used to define the molecular surface of each cluster. The bond order indices (b_ϵ) reported in this study were obtained from the energy as:

$$b_\epsilon = \frac{\epsilon_{\tau AB}^S(\vec{r}_{\text{Lagrange}})}{\epsilon_{\tau HH}^S(\vec{r}_{\text{Lagrange}})} \quad (49)$$

where $\epsilon_{\tau AB}^S(\vec{r}_{\text{Lagrange}})$ and $\epsilon_{\tau HH}^S(\vec{r}_{\text{Lagrange}})$ are the energy densities at the Lagrange points of the bond of

interest A-B and the H-H bond of H_2 molecule, respectively. The regional electronic chemical potential μ_R is obtained from the ratio of energy density to electronic density [25,26]. Electron deformation density plots are shown for the $0.022e/\text{\AA}^3$ iso-surface. VMD [32] and PyMol [33] were used for visualization of electronic stress tensor, bond indices and chemical potential.

5.3 Results and Discussion

5.3.1 Bonding in Ga_2

Previous studies have suggested that the structures of gallium clusters and the α -gallium bulk phase are strongly influenced by the tendency for gallium to form Ga_2 subunits [6, 19]. It is therefore of interest to apply electron deformation density and RDFT analysis to investigate the bonding in Ga_2 before exploring the bonding in the $Ga_{12}X$ clusters. The electron deformation density identifies regions that have high electron density as a result of bonding interactions in the molecule or cluster. Figure 2 includes a plot of the electron deformation densities for the ground state ($^3\Pi_u$) and first triplet-excited-state ($^3\Sigma_g^-$) of Ga_2 .

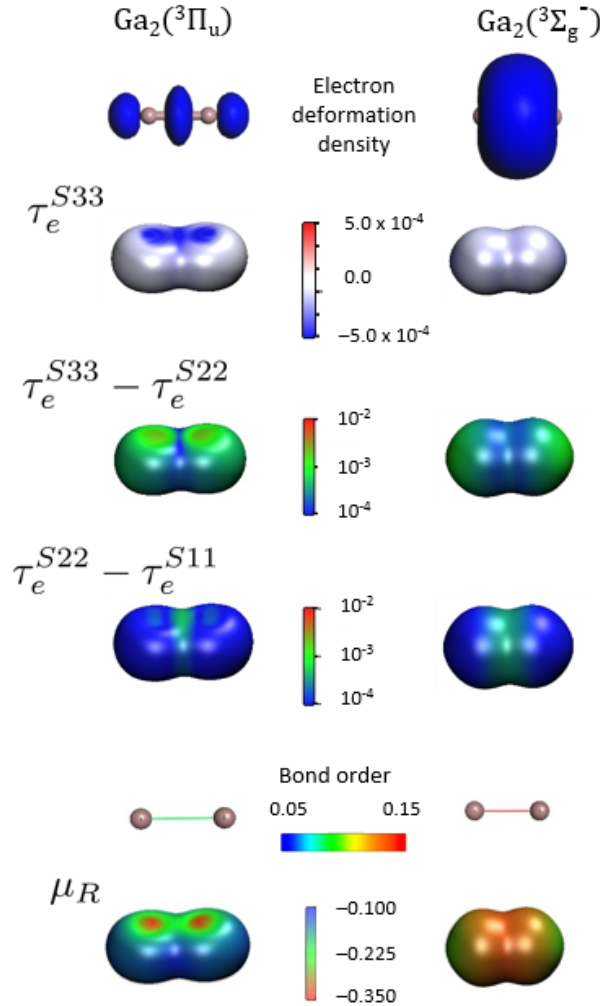


Fig. 2: RDFT analysis of Ga_2 in the ground ($^3\Pi_u$) and first triplet excited ($^3\Sigma_g^-$) states.

The equilibrium bond length of the Ga_2 molecule arises from a balance between the competing atomic orbital interactions required to form the molecular orbitals. As noted in the Introduction, the

long bond length of the ${}^3\Pi_u$ electronic state arises largely from the σ overlap requirements of the $4p_x$ orbitals that form the $2\sigma_g^+$ molecular orbital. However, the long interatomic distance weakens the bonding interaction between the $4p_y$ orbitals. Consequently, the $2\sigma_g^+$ molecular orbital is lower in energy than the π_u orbital and therefore makes a greater contribution to the bond energy in the ${}^3\Pi_u$ electronic state. The electron deformation density for the ground state of Ga_2 has the same spatial distribution as the $2\sigma_g^+$ molecular orbital, reflecting the contribution this orbital makes to bonding in the ground state. In comparison, the electron deformation density of the ${}^3\Sigma_g^-$ state is uniform and cylindrical, reflecting the equal contributions of the two singly occupied π_u orbitals to the bonding in this state.

The electronic stress method [23–26] provides information about the localization of electrons between pairs of atoms within a molecule. We denote the three eigenvalues of the electronic stress tensor in the ordering as follows: $\tau_e^{S33} \geq \tau_e^{S22} \geq \tau_e^{S11}$. If τ_e^{S33} is positive this corresponds to tensile stress and indicates localisation of electrons in these regions i.e. covalent character between a pair of atoms. However, if τ_e^{S33} is negative this corresponds to compressive stress, which generally indicates delocalization of the electrons in this region. This type of stress is observed in both metallic bonds and in short $\text{C} \equiv \text{C}$ triple bonds of alkynes, due to the high concentration of electron density.

Figure 2 also displays maps of τ_e^{S33} on the electronic interface of the ${}^3\Pi_u$ and ${}^3\Sigma_g^-$ states of Ga_2 . The variations in these maps correlate with the net bonding contributions arising from the valence $4p$ orbitals. It is clear that in the ${}^3\Pi_u$ state, τ_e^{S33} is very slightly negative across most of the surface of the molecule indicating that the electrons are not strongly localized. Furthermore there is a noticeable area of more negative τ_e^{S33} character, indicating compressive stress, in the bridge region along the x - y plane of the molecule. This arises from a weak bonding contribution from the singly occupied π_u molecular orbital due to poor overlap of the $4p_y$ valence orbitals at the interatomic distance of $2.71\text{\AA}$. In comparison, the plot for the ${}^3\Sigma_g^-$ state exhibits a uniform τ_e^{S33} surface with no specific regions of high compressive stress. This is consistent with the stronger bonding in the π_u molecular orbitals due to greater overlap of the $4p_y$ and $4p_z$ valence orbitals at the shorter interatomic separation of this electronic state ($2.45\text{\AA}$).

The differential eigenvalues $\tau_e^{S33} - \tau_e^{S22}$ and $\tau_e^{S22} - \tau_e^{S11}$ can be used to quantify degeneracy amongst the three eigenvalues of the stress tensor, which can highlight important features of the different types of bonding. Covalent bonds exhibit strong directionality with one positive eigenvalue substantially larger than the other two. Covalent bonding in hydrocarbons is reflected by $\tau_e^{S33} - \tau_e^{S22}$ values in the range $0.1 - 1$ and $\tau_e^{S22} - \tau_e^{S11}$ values in the range $0 - 0.04$. In comparison, the strong metallicity of the alkali metal species is demonstrated by the very small values obtained for both $\tau_e^{S33} - \tau_e^{S22}$ and $\tau_e^{S22} - \tau_e^{S11}$. Figure 2 displays maps of the differential eigenvalue $\tau_e^{S33} - \tau_e^{S22}$ on the electronic surface of the two lowest energy triplet electronic states of Ga_2 . The $\tau_e^{S33} - \tau_e^{S22}$ differential eigenvalues for the ${}^3\Pi_u$ state vary across the molecule with the smallest values at the centre of the bond and a gradual increase in the values moving away from the bonding region. This indicates that τ_e^{S33} and τ_e^{S22} are almost degenerate in the centre of the molecule but differ at the axial extremes of the molecule. In comparison, $\tau_e^{S22} - \tau_e^{S11}$ values are largest at the centre of the bond and decrease moving away from the bond, indicating that the τ_e^{S22} and τ_e^{S11} are degenerate across most of the molecular surface. Again, this pattern is consistent with net bonding contributions arising from the singly occupied $2\sigma_g^+$ and π_u orbitals of the ground state. In particular, the $2\sigma_g^+$ orbital is bonding along the molecular axis with large lobes also located outside the bond, which corresponds with the largest $\tau_e^{S33} - \tau_e^{S22}$ values. In comparison, the π_u orbital does not lead to strong localization of the electron in the interatomic region and this contributes to the small $\tau_e^{S33} - \tau_e^{S22}$.

The $\tau_e^{S33} - \tau_e^{S22}$ values for the ${}^3\Sigma_g^-$ state exhibit a similar distribution to that of the ${}^3\Pi_u$ state but the small values extend further from the centre of the bond and the values in the axial atop regions are larger than for ${}^3\Pi_u$ state. This is consistent with a bond consisting primarily of π -character. The $\tau_e^{S22} - \tau_e^{S11}$ differential values indicate that $\tau_e^{S22} - \tau_e^{S11}$ are degenerate across most of the molecular surface.

As noted in the Introduction, the long bond length of the ground state of Ga_2 largely arises from a need to balance the nuclear repulsion energy with the competing sigma and pi overlap requirements of the $4p_x$ and $4p_y$ orbitals. In the $^3\Sigma_g^-$ excited state, net bonding arises from the two degenerate π_u orbitals, which are formed from equivalent overlap of the $4p_y$ and $4p_z$ orbitals, leading to a shorter bond length. Consequently, the energy density bond order is slightly higher for the $^3\Sigma_g^-$ state than for the $^3\Pi_u$ state. Nevertheless, both values are substantially smaller than the unity value found for the fully covalent σ -bond of H_2 . The behavior in both of these electronic states of Ga_2 , indicates bonding character that is intermediate between covalent and metallic, consistent with other semi-metal systems [34, 35]. Inspection of the chemical potential plots indicates that the most electrophilic region of the $^3\Pi_u$ state is the bridge region, which facilitates the addition of hydrogen across the Ga – Ga bond as in Ga_2H_6 . The $^3\Sigma_g^-$ state is electrophilic near the centre of the bond with values decreasing slightly moving away from the bond.

5.3.2 Structure and Bonding of endo- Ga_{12}X

As reported previously [10, 36–38], the pure Ga_{13} cluster has a distorted decahedral structure. Consequently, the two 5-membered rings in the equatorial region of the cluster are in an eclipsed arrangement so that each of these Ga atoms has a nearest neighbor in the opposing ring at $\sim 2.6\text{\AA}$. These pairs of atoms can be considered as Ga_2 subunits. Our earlier study [14] explored an extensive range of endohedral doped isomers including icosahedral and decahedral structures. For clusters doped with third- and fourth-row p-block elements the structures with decahedral-like symmetry were identified as the lowest in energy. The Ga_{12}Si and Ga_{12}Ge clusters have 40 valence electron configurations, which corresponds with a stable closed shell electronic configuration within the Jellium model and therefore they exhibit the most compact structures. In comparison, when doping the core of the clusters with second-row p-block dopants the isomers with icosahedral-like symmetry are lowest in energy, with the 40-electron cluster (endo- Ga_{12}C) again being the most compact of the three clusters.

The deformation densities for the icosahedral gallium clusters with $\text{X} = \text{B}, \text{C}$ or N , generally have the same features as the isoelectronic Al_{12}X clusters (Fig. 3a). In particular, the electronic charge forms a framework throughout the cluster with the highest densities located in the interstitial regions. This corresponds with development of metallic or Jellium-like bonding and compares well with earlier studies of Al_{13} , Al_{13}^- and Al_{12}Si [39–43]. As reported previously this is also evidenced by the high degree of degeneracy in the eigenvalue spectrum of Ga_{12}C [10, 44]. In addition to the delocalised framework, there is significant charge concentrated about the core atom of these endo- Ga_{12}X clusters. Sun et al. [33] noted similar behaviour for Al_{12}Si , with the excess charge from the core silicon atom distributed in bonds between the core and the cage Al atoms. As the electronegativity of the core atom increases these regions of electron density become more contracted.

The deformation density isosurfaces of endo- Ga_{12}X clusters with third- and fourth-row dopants are quite different, with delocalised metallic framework only observed between the axial and equatorial atoms. In comparison, there is a small region of very localised charge density in the centre of each of the Ga_2 subunits of the equatorial region. This localised density is very similar to the bonding in the ground state of Ga_2 and is evidence of residual covalent character between these atoms. These clusters also exhibit a concentration of charge about the core dopants, which becomes more contracted with electronegativity of the dopant atom. Consequently, this region of density is least contacted in the endo- Ga_{12}Al and Ga_{13} clusters and in fact merges with the delocalised density of the axial regions and to a lesser with the density of the Ga_2 sub units. We have shown previously [10] that endo- Ga_{12}X clusters with $\text{X} = \text{Al}, \text{Si}, \text{Ga}$ and Ge , are less Jellium-like than their icosahedral counterparts and this is consistent with the less developed electron deformation density framework observed in these species.

Figure 3(b) displays maps of τ_e^{S33} on the electronic interface of endohedral gallium clusters. As can be seen from these maps, τ_e^{S33} has a slightly negative value across most of the surface, indicating slight compressive stress throughout the clusters. The most negative (blue) regions are located in the

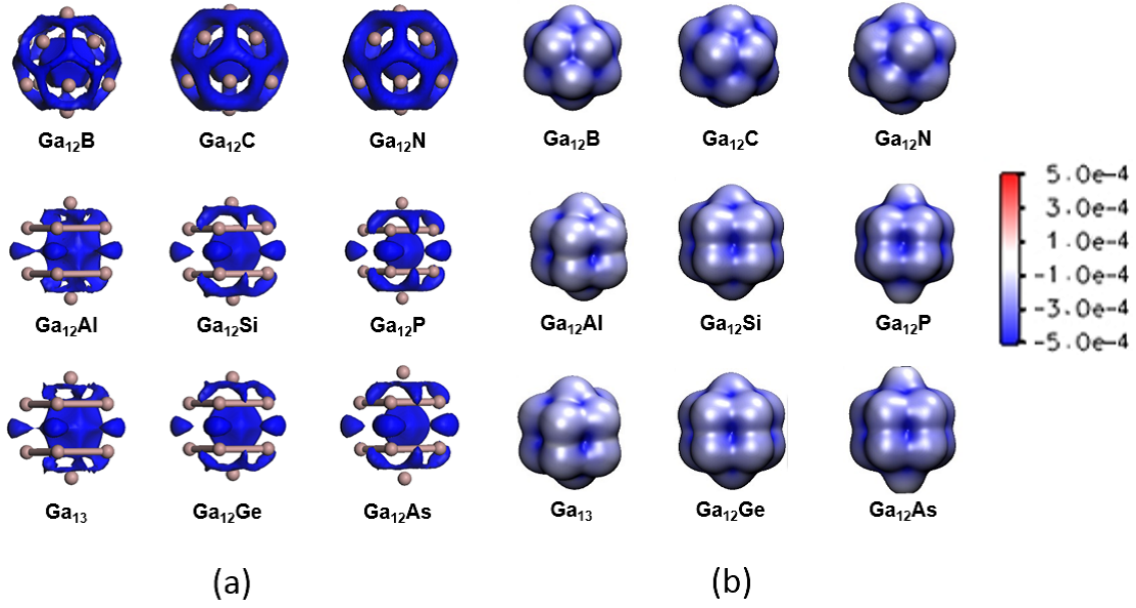


Fig. 3: (a) Electron deformation densities for endohedral Ga_{12}X clusters and (b) Maps of τ_e^{S33} on the electronic interfaces of endohedral gallium clusters.

centre of the hollow faces of the clusters indicating significant delocalisation of the electron density in these regions, which generally correlates well with the regions of highest electron density in the electron deformation density plots (Fig. 3a). However, in the bridge locations between pairs of atoms, the τ_e^{S33} values are only slightly negative suggesting that the electrons are not fully delocalised and bonding is intermediate between covalent and metallic. Figure 3b also suggest that the Ga_2 subunits of the decahedral clusters show the least metallic character, particularly for the 39 valence electron clusters (Figure 3(a)). In fact the τ_e^{S33} surfaces for each of these pairs of atoms bear a close resemblance to the τ_e^{S33} surface of the $^3\Pi_u$ state of Ga_2 . In comparison, τ_e^{S33} values between atom pairs of the icosahedral clusters are quite uniform across the surfaces of the clusters. However, the variations in τ_e^{S33} surfaces suggest an increase in metallic character from Ga_{12}B through to Ga_{12}N .

Covalent bonds are identified within the RDFT scheme by a positive largest eigenvalue and strong directionality. The recent study on lithium clusters has shown that metallic bonding is characterized by negative values for the three eigenvalues of the electronic stress tensor, with no particular directionality [23]. Metalloid bonds generally exhibit slightly negative eigenvalues with some directionality. Figure 4 displays a plot of τ_e^{S33} at the Lagrange points of Ga cluster bonds versus bond length. As noted above the τ_e^{S33} values are generally slightly negative and therefore intermediate between fully covalent and metallic i.e. they are metalloid. However, the magnitude of the τ_e^{S33} values decreases with bond length. In fact there is almost a linear correlation between τ_e^{S33} and bond length for the surface Ga-Ga bonds of the endo- Ga_{12}X clusters. Therefore the longest bonds exhibit the least delocalization of the local electron density, which would correspond with less π -character between these atoms. The Ga-X bonds for the endohedral doped clusters with decahedral symmetry ($\text{X} = \text{Al}, \text{Si}, \text{P}, \text{Ga}, \text{Ge}$ or As) exhibit similar behaviour to Ga-Ga bonds. In comparison, the Ga-X bonds of endo- Ga_{12}B , endo- Ga_{12}C and endo- Ga_{12}N are found to have τ_e^{S33} values very close to zero and therefore exhibit less delocalization of the electron density than a Ga-Ga bond of the same length. This corresponds with the concentration of charge about the core dopants of these icosahedral-like clusters.

The $\tau_e^{S33} - \tau_e^{S22}$ values, which shown in Figure 5(a), are generally quite small across the surfaces of the clusters. However, $\tau_e^{S33} - \tau_e^{S22}$ values in atop positions are an order of magnitude higher than those of the hollow positions. The eigenvalue maps also indicate that the Ga_2 subunits of the equatorial region

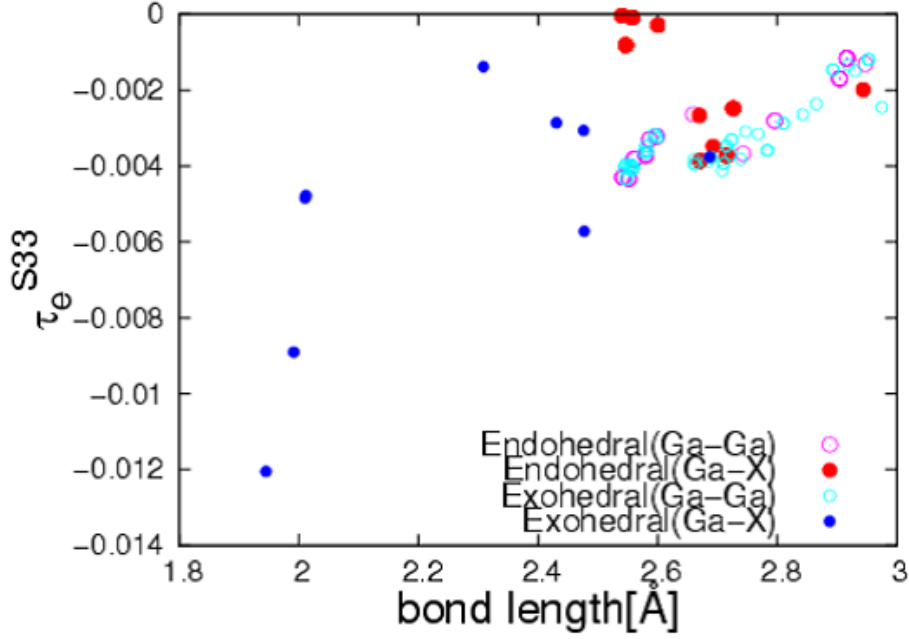


Fig. 4: Plot of τ_e^{S33} versus bond length for gallium clusters (Ga_{12}X).

exhibit the least degeneracy between τ_e^{S33} and τ_e^{S22} which is indicative of more covalent character in these regions. Maps of the $\tau_e^{S22} - \tau_e^{S11}$ differential eigenvalue (Figure 5(b),) also highlight the difference in bonding between atoms of the Ga_2 subunits and other atomic pairs in these clusters.

Figure 6(a) provides a plot of $\tau_e^{S33} - \tau_e^{S22}$ vs $\tau_e^{S22} - \tau_e^{S11}$ values for a range of different species including covalently bonded hydrocarbons, alkali metal clusters, aluminium clusters and our doped gallium clusters.

Covalent bonding in hydrocarbons is reflected by $\tau_e^{S33} - \tau_e^{S22}$ values in the range 0.1 – 1 and $\tau_e^{S22} - \tau_e^{S11}$ values in the range 0 – 0.04. In comparison, the strong metallicity of the alkali metal species is demonstrated by the very small values obtained for both $\tau_e^{S33} - \tau_e^{S22}$ and $\tau_e^{S22} - \tau_e^{S11}$. Tachibana and co-workers [25,26] have shown previously that in semimetal species such as Aln clusters and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST), the bonding is intermediate between covalent and metallic. The differential eigenvalues for our gallium clusters also clearly fall in this semimetal range. Figure 5b displays an enlargement of the region of the alkali and semimetal species. Although the Ga_{12}X cluster values are in the same region as the values for Al clusters and GST, there are subtle differences between the systems. For example, aluminium clusters exhibit only a small range of $\tau_e^{S33} - \tau_e^{S22}$ values but a large range for $\tau_e^{S22} - \tau_e^{S11}$. In comparison, our Ga_{12}X clusters exhibit a large spread of $\tau_e^{S33} - \tau_e^{S22}$ values but a small spread of $\tau_e^{S22} - \tau_e^{S11}$ values. This again reflects the differences in bonding between the Ga_2 subunits and the other atomic pairs within the clusters.

Energy density bond indices (b_e) were calculated where Lagrange points could be located between adjacent atoms and are shown as coloured lines in Figure 6.

Significant differences can be seen between the group of clusters with second-row dopants and those with third- and fourth-row dopants. Firstly, for the endo- Ga_{12}B , endo- Ga_{12}C and endo- Ga_{12}N clusters, Lagrange points were only identified inside the clusters, between the core dopant and the surface gallium atoms. This is the same region as the concentrated charge identified in the deformation densities and coincides with the Jellium 1P and 2P shells that are composed of bonding orbitals between the core and the surface. It is clear from the b_e bond-order plots that the largest bond order indices are found in the highly stable 40 valence electron cluster, endo- Ga_{12}C , followed by the endo- Ga_{12}N and then the endo- Ga_{12}B clusters. The 1P and 2P shells are well developed in these clusters and the bond indices

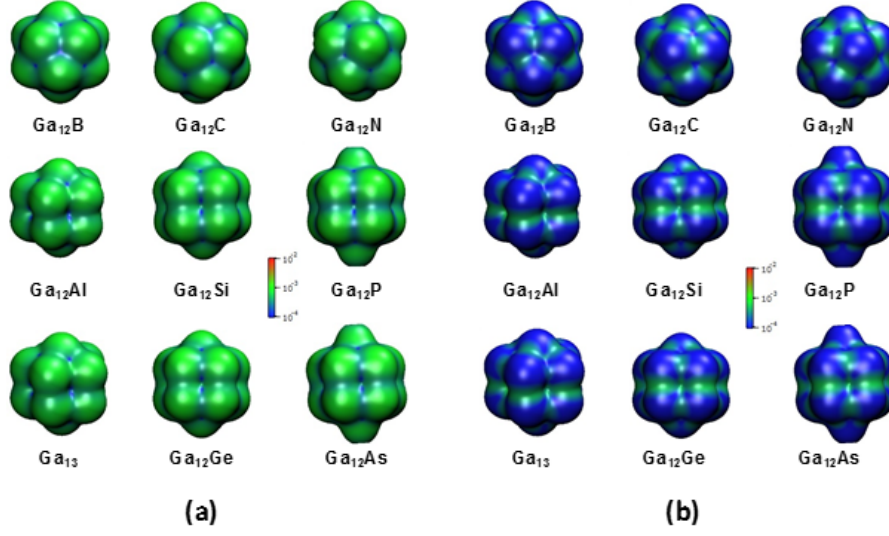


Fig. 5: Maps of (a) $\tau_e^{S33} - \tau_e^{S22}$ and (b) $\tau_e^{S22} - \tau_e^{S11}$ differential eigenvalues, on the electronic interfaces of endohedral doped gallium clusters.

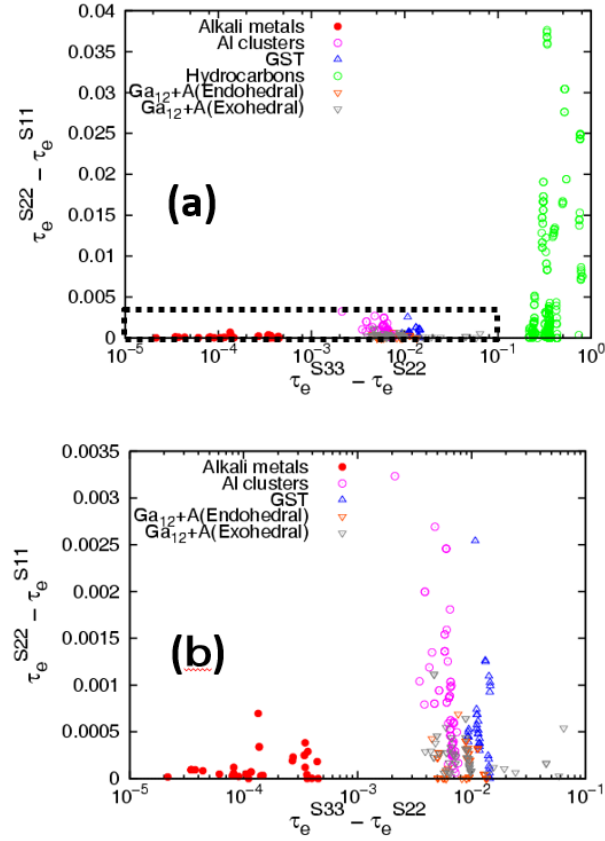


Fig. 6: (a) Plots of $\tau_e^{S33} - \tau_e^{S22}$ vs $\tau_e^{S22} - \tau_e^{S11}$ for a range of different species and bond types and (b) an enlargement of the metal and semimetal region.

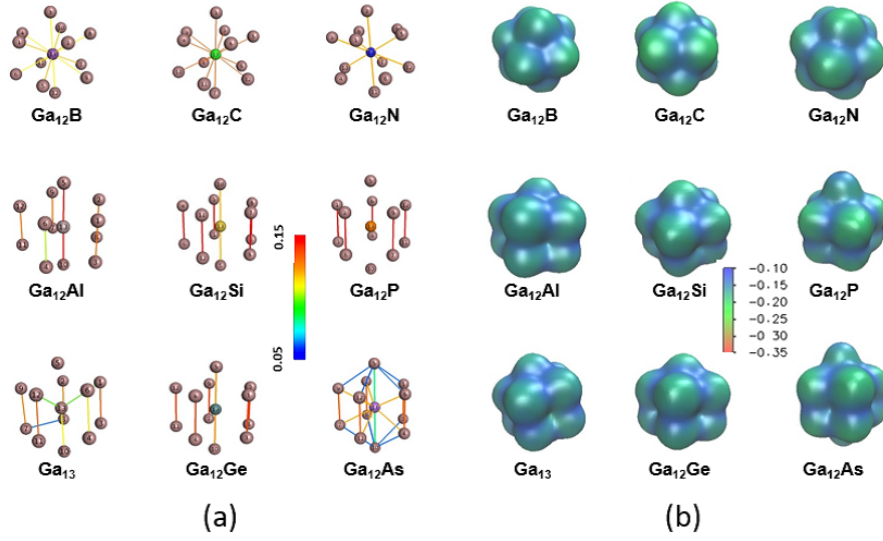


Fig. 7: (a) Energy density bond indices (b_ϵ) and (b) maps of electronic chemical potential for endohedral doped (Ga_{12}X) clusters.

correlate with the increasing degeneracy in each of these sets of orbitals. Nevertheless, we find bond indices of only $\sim 10\%$ of the value of the H-H bond and this reflects only a low level of covalency between core and surface atoms.

The endo- Ga_{12}X clusters with third and fourth row dopants have lower symmetry than the icosahedral-like clusters described above and exhibit quite different patterns of bond indices. In particular, relatively few Lagrange points were located inside the clusters, which coincides with breaking of the degeneracy in the 1P and 2P Jellium shells. In contrast, many Lagrange points were located between pairs of surface atoms, particularly for the Ga_2 subunits of these clusters. The bond indices for the equatorial Ga_2 subunits of Ga_{12}Al , Ga_{12}Si and Ga_{12}P follow the pattern of bond lengths. For example, in Ga_{12}Al one of the Ga_2 subunits is elongated relative to the other four and this pair of atoms have a significantly weaker bond. In comparison the equatorial Ga_2 bonds of the Ga_{12}Si and Ga_{12}P clusters are consistently stronger. There is a systematic decrease in the bond indices between the dopant X and the axial gallium atoms across this series of clusters. These patterns of bond indices are consistent with the observed regioselectivity for hydrogen adsorption on the cluster surfaces [21]. For example, in Ga_{12}Al the highest reactivity is generally observed in the region of the Ga_2 subunits, which have weaker bonding than the axial Ga-X bonds. The Ga_{12}Si and Ga_{12}P have increased reactivity in the axial regions due to a weakening of the axial Ga-X bonds, while decreases in reactivity at the equatorial Ga_2 sub units correspond with increases in bond index. Both the bond indices and the regioselectivity can be understood in terms of the occupations of the frontier orbitals of these clusters. Due to a Jahn-Teller distortion, the HOMO of the 39 valence electron clusters is a singly occupied bonding orbital located in the equatorial region. The lobes of this orbital correspond with the Ga_2 subunits. In the 40 valence electron clusters, the HOMO is doubly occupied and part of the degenerate set of Jellium orbitals, which increases the bonding character and the bond indices in the Ga_2 subunits. In the 41 valence electron systems, there is opening of the next Jellium shell. This again leads to a Jahn-Teller distortion, in this case along the axis of the cluster, which results in a weakening of the bonding in the Ga_2 subunits. However, again we find that the average b_ϵ values in our endo- Ga_{12}X clusters are $\sim 5 - 15\%$ of the value for the H-H bond indicating only a low level of covalency.

The overall features of the bonding in the fourth-row doped clusters are generally similar to the third-row doped species but the b_ϵ are generally smaller. This can be linked to the larger size of the

core atoms in these clusters that induces strain in the Ga_{12} cage. For example, the Jahn-Teller distortion in Ga_{13} is larger than in Ga_{12}Al , leading to a broader distribution of b_e values for the Ga_2 subunits. Furthermore, the core Ga is not located equidistant from both axial atoms therefore these bonds have different bond indices. The bonding patterns for Ga_{12}Ge and Ga_{12}As closely reflect those of Ga_{12}Si and Ga_{12}P , respectively, but as noted above, the absolute b_e values are slightly smaller.

The chemical potential (μ) maps identify variations in electrophilicity across the surface of the clusters (Fig. 6b). Regions with higher electrophilicity are identified with more negative μ values, whereas regions with weaker μ (less negative) are generally more nucleophilic. It is clear from Figure 6b that the atop positions of all of the endo- Ga_{12}X clusters exhibit the most negative μ values and therefore are the most electrophilic regions of the clusters. Comparison across a series reveals that the surface atoms are increasingly deshielded with increasing electronegativity of the core atoms, reflecting the transfer of charge density towards the core. In comparison, the bridge and hollow positions of the clusters have less negative μ values and can be considered more nucleophilic. In general, hydrogen atom is adsorbed in electrophilic regions of the clusters. As the electronegativity of the core dopant increases, so does the electrophilicity of the surface and the bonding to H atom becomes increasingly more localised. Consequently, adsorption in equatorial fourfold hollow sites is only observed in the Ga_{13} and endo- Ga_{12}Al clusters. In comparison, the endo- Ga_{12}P and endo- Ga_{12}As clusters exhibit a clear preference for localized bonding to H atom in the axial and equatorial atop positions. The endo- Ga_{12}Si and endo- Ga_{12}Ge clusters are intermediate between these two extremes.

5.3.3 Structure and Bonding of exo- Ga_{12}X

In this section we discuss the trends in the bonding of exohedrally doped gallium clusters (exo- XGa_{12}). The exo- Ga_{12}X isomers have similar cage structures to their endohedral counterparts. Nevertheless, locating the dopant in the cluster surface leads to a loss of symmetry and generally destabilises the clusters relative to the corresponding endo- Ga_{12}X isomers [20]. In the case of $\text{X} = \text{Al}$, the destabilisation is marginal (+0.02 eV), whereas for $\text{X} = \text{P}$ and Si , the effect is quite large (+0.40 and +0.61 eV). Lighter element exohedral dopants introduce significant structural distortion but the energetic effect is element specific. For example, the exo- CGa_{12} isomer is significantly higher in energy (+0.70 eV) than endo- Ga_{12}C , whereas exo- NGa_{12} is slightly lower in energy (-0.10 eV) than endo- Ga_{12}N .

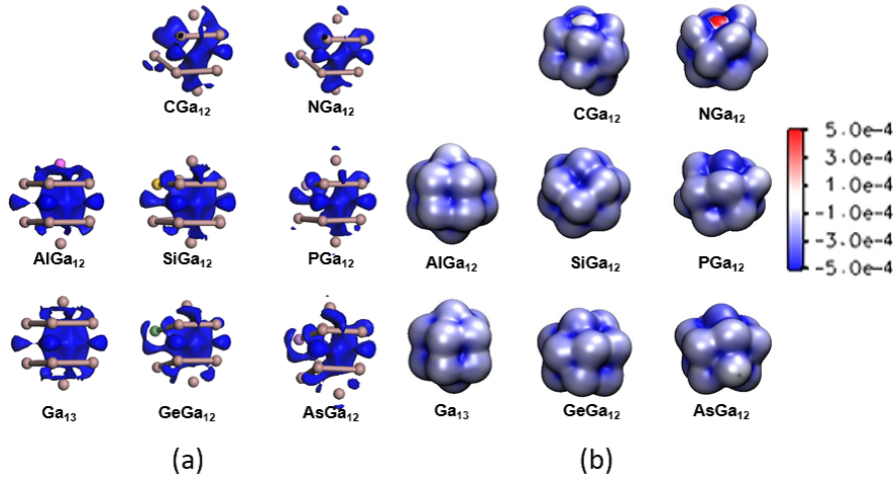


Fig. 8: (a) Electron deformation densities ($0.02 \text{ electrons } \text{\AA}^{-3}$) for exohedral Ga_{12}X clusters and (b) Maps of τ_e^{S33} on the electronic interfaces of exohedral gallium clusters.

Comparison of Figures 3(a) and 8(a) reveals that the deformation density of exo- AlGa_{12} is quite

similar to that of endo-Ga₁₂Al and the undoped Ga₁₃, with delocalised bonding throughout the core and the axial region and localised bonding at the centre of the Ga₂ subunits. This indicates that the axial aluminium dopant exerts only a small perturbation on the bonding of the system. The deformation densities of the equatorial doped exo-SiGa₁₂ and exo-GeGa₁₂ clusters differ significantly from their endohedral counterparts but bear similar features to exo-AlGa₁₂. These include delocalised charge throughout the core region that extends to the axial region and charge density at the centre of the Ga₂ subunits. However, there is concentration of charge around the dopant site of each of these cluster reflecting their greater electronegativity. The redistribution of charge density towards the dopant is further enhanced in the exo-PGa₁₂ and exo-AsGa₁₂ clusters so that there is a significant reduction in charge density in the axial regions which corresponds with the weakening and lengthening of the X-Ga_{ax} bonds. Charge density is also concentrated around the dopant atoms in exo-CGa₁₂ and exo-NGa₁₂ and this substantially disrupts the bonding, leading to significant distortion of the cluster symmetry.

Figure 7b displays maps of τ_e^{S33} on the electronic interface of exohedral gallium clusters. As for the endohedral-doped clusters, τ_e^{S33} generally has a slightly negative value across most of the surface, indicating compressive stress throughout the clusters. For most of this group of clusters, the most negative (blue) regions are located in the centre of the hollow faces of the clusters indicating significant delocalisation of the electron density in these regions. The τ_e^{S33} values are generally only slightly negative in the bridge locations, suggesting that the electrons are not fully delocalised and bonding is intermediate between covalent and metallic. However, for some clusters the presence of the dopant at the surface does lead to some significant local effects. For example, τ_e^{S33} is close to zero around the aluminium atom of exo-AlGa₁₂ and the carbon atom of exo-CGa₁₂ indicating less delocalisation of electrons in this region relative to the other regions of the cluster surface. We also find that τ_e^{S33} is positive around the nitrogen atom of exo-NGa₁₂ indicating localised covalent bonding. In comparison, τ_e^{S33} is negative around the P and As atoms of exo-PGa₁₂ and exo-AsGa₁₂, respectively, indicating increased delocalisation of electrons in these regions.

As for the endohedral clusters, the magnitude of the τ_e^{S33} values for Ga-Ga bonds of the exohedral clusters decrease almost linearly with increasing bond length (Fig. 4). In comparison, the τ_e^{S33} values for Ga-X bonds of these clusters exhibit a less systematic variation. The values that show the largest deviation from the linear trend are the short Ga-C bonds of the exo-CGa₁₂ cluster and to a lesser extent the Ga-N bonds of exo-NGa₁₂. The more negative τ_e^{S33} values of these clusters imply metallic bonding in these regions. However, this may also be due to the high concentration of electron density in these regions.

The $\tau_e^{S33} - \tau_e^{S22}$ values which shown in Figure 9(a), are generally quite small across the surfaces of the clusters and indicate that electrons are delocalised in the hollow regions of each cluster and around the Al atom of exo-AlGa₁₂. In comparison, there is an increase of electron localisation around the carbon and nitrogen atoms of exo-CGa₁₂ and exo-NGa₁₂. The $\tau_e^{S22} - \tau_e^{S11}$ differential eigenvalues are very small across most of the surface of the clusters, with the largest values identified between Ga atoms of the Ga₂ subunits and between the dopants and neighbouring gallium atoms of exo-CGa₁₂ and exo-NGa₁₂. Figure 5 includes a plot of $\tau_e^{S33} - \tau_e^{S22}$ vs $\tau_e^{S22} - \tau_e^{S11}$ values for exohedral-doped clusters. The values for the exohedral clusters fall in the same region as the endohedral clusters, again implying that overall the bonding in these species is intermediate between covalent and metallic.

The exo-XGa₁₂ clusters with third and fourth row dopants have similar distributions of bond indices to their endohedral counterparts (Fig. 8a). In particular, equatorial Ga-Ga bonds generally have larger b_ϵ values than the axial Ga-X bonds. The systems with second-row dopants exhibit significant distortion away from the icosahedral symmetry, which can be understood by the preference to form strong short bonds between the dopant and the neighbouring gallium atoms. This leads to a weakening of many of the other bonds throughout the cluster relative to corresponding endo-Ga₁₂X clusters.

The chemical potential maps for the decahedral-like exo-XGa₁₂ clusters indicate that the surface gallium atoms are generally deshielded, making these regions electrophilic (Fig. 8b). Bridge positions tend to be less electrophilic than the atop positions. The largest differences in chemical potential are

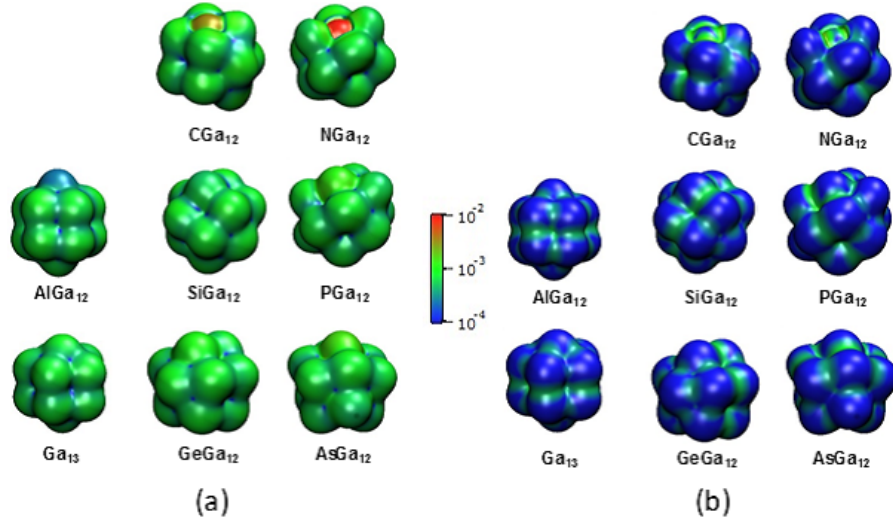


Fig. 9: Maps of (a) $\tau_e^{S33} - \tau_e^{S22}$ and (b) $\tau_e^{S22} - \tau_e^{S11}$ differential eigenvalues, on the electronic interfaces of exohedral doped gallium clusters.

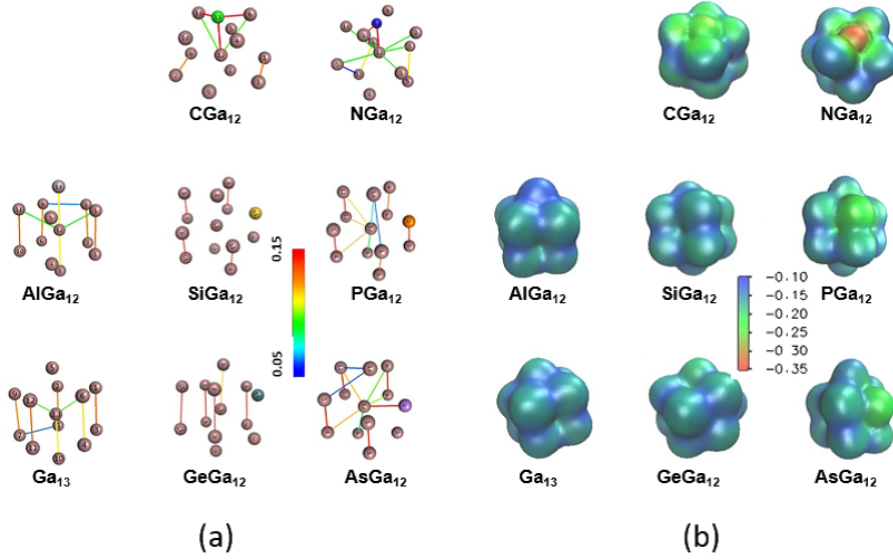


Fig. 10: (a) Energy density bond indices (b_ϵ) and (b) maps of electronic chemical potential μ_R for exohedral doped (XGa₁₂) clusters.

observed around the dopant atoms. For the exo-XGa₁₂ clusters, μ becomes successively more negative around the dopant for the series X = Al, Si and P, with the Al atom being less electrophilic and P being substantially more electrophilic than the surface gallium atoms of the respective clusters. A similar trends is observed for the X = Ga, Ge, As series of clusters but the μ values around the X atoms are generally slightly smaller in magnitude. The region around the dopant atoms of exo-CGa₁₂ and exo-NGa₁₂ are also highly electrophilic.

5.4 Conclusion

Electron deformation density plots and Regional Density Functional Theory (RDFT) have been used in this study to investigate the bonding of Ga₂ and Ga₁₂X clusters. Clear differences are identified in the bonding characteristics of the ground (³Π_u) and first excited triplet (³Σ_g⁻) states of Ga₂ that can be used to identify the presence of Ga₂ subunits in larger clusters.

The electronic properties of the icosahedral based endo-Ga₁₂X clusters with second-row p-block dopants are generally very similar to isoelectronic Al₁₂X clusters. The small size of the core dopant in these systems combined with their electronegativity relative to gallium results in charge being transferred from the surface atoms towards the core. The concentration of charge between the core and the surface atoms provides evidence for the establishment of a metallic or Jellium-like bonding in these species.

The larger size and smaller electronegativity of 3rd and 4th row dopants, relative to gallium, leads to quite a different charge distribution in the endo-Ga₁₂X clusters with X = Al, Si, P, Ge or As. Although there is electron delocalisation around the core and axial regions of these clusters, there is also strong evidence of Ga₂ subunits in the equatorial region.

RDFT analysis of the endo-Ga₁₂X clusters reveals bond properties intermediate between metallic and covalent, consistent with semimetal materials. The RDFT analysis also reveals similarities between the bonding in the Ga atoms of the equatorial region of the endo-Ga₁₂X clusters and the ground state of the Ga₂ molecule. The calculated b_e bond indices and surface maps of electronic chemical potential provide understanding for the previously observed regioselectivity for hydrogen atom adsorption [15]. The significant deshielding around the surface atoms, caused by migration of charge towards the core, suggests that these clusters will interact strongly with nucleophiles and Lewis bases. These results clearly explain the previously reported variations in regioselectivity for H atom adsorption across this series of clusters.

Exohedral doping with second-row p-block dopants leads to a large concentration of charge density around the dopants that significantly distorts the cluster geometry. The third- and fourth-row elements (X = Al, Si, P, Ge and As) generally cause only a minor perturbation to the geometry of the cluster when used as exohedral dopants. This can again be attributed to their similar size and electronegativity to gallium. RDFT analysis reveals that the surface atoms of the exo-XGa₁₂ clusters are also generally deshielded and therefore electrophilic. This is most evident in the region of the dopants.

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Chapter 6

6 Tension Density as Counter Force to the Lorentz Force Density

6.1 Introduction

Materials for semiconductor devices are now designed in nanometer scale as a result of the rapid progress of technology. The accurate prediction of conduction property of materials is useful for the design of nanosize devices. For example, the conductance of nanosize materials is frequently reported by experimental and theoretical studies. In the theoretical studies of these nanosize materials, we must include quantum effects for correct understanding. Quantum mechanics is widely used for the studies because it is easy to use. However, in quantum mechanics, electromagnetic fields are treated as classical external fields, and particularly only a scalar part in four component vector potential is included in most studies. In other words, quantum mechanics is not consistent with Maxwell equation, though we want to investigate electrical conduction, that is, electromagnetic phenomena. In quantum electrodynamics (QED), which is defined in quantum field theory, electromagnetic fields are treated as quantum photon fields and quantum states are consistent with Maxwell equation. Therefore, we consider these electric device materials to be studied in terms of QED. In another merit of QED, a physical quantity can be treated as a local quantity since this theory is quantum field theory, while in quantum mechanics a physical quantity is defined as an expectation value integrated over the whole region. For nanosize materials, we consider that ordinary global and averaged quantities are not suitable for studying their properties, since it is known that a physical quantity of these materials is dominated by defects, impurities, or an interface. Hence in order to investigate these effects, the effects of these local objects should be analyzed in a quantitative form.

From this viewpoint, we have proposed the analysis of nanosize materials by Rigged QED [1–3]. Rigged QED is QED with the inclusion of nuclei in a gauge invariant way. In Rigged QED, a physical quantity can be analyzed as a local density quantity. Previously we have studied, for example, local dielectric constant and polarizability [4–10], and local spin torque [11–14]. For the study of the local conductive properties of nanosize materials, local conductivity tensors have been used [12, 15–19]. In our previous works, we have demonstrated the computation of the distribution of the local current density and proposed that the local conductivity [1, 2] is suitable for the analysis for nano-size materials.

In this work, the Lorentz force, which is the driving force for the conduction of electrons, is studied as local density force. It is numerically confirmed that for an equilibrium current the acceleration by the Lorentz force density is balanced with the deceleration by the tension density defined in Rigged QED at any point. In other words, the tension density is the counter force to the Lorentz force. This balance is explained in classical mechanics, for example in the Drude model, by the assumption of the introduction of the phenomenological friction term [20]. This friction is assumed to be brought by scattering and parametrized as the mean free time, that is, the relaxation time. A quantum treatment of transport of electron is described by Boltzmann equation [21]. In this treatment, the Lorentz force is balanced with diffusion and scattering. However, this results in a complicated integro-differential equation and it seems to be hardly solved except for simple cases, and the relaxation time parametrization is often used too. In Landauer’s and Kubo’s theories, a conductance is derived through a transmission coefficient without the assumption of the friction, while a specific counter force is not paid attention to in the theories. On the other hand, our tension density is introduced from the equation of motion of the kinetic momentum in QED. In addition, it can be calculated using state vectors and hence we can easily handle it.

Previously, using the tension density, new views on chemical bonding have been proposed [1–3, 22–25]. We have shown that the “Lagrange point”, the point between two atoms where the tension density vanishes, can well characterize the chemical bond between them [26, 27]. We have also shown that the “Lagrange surface”, separatrices of the tension density vector field, may define boundary surfaces of

atoms in a molecule [2, 24, 28–30]. In addition, it is pointed out that the eigenvalues and corresponding eigenvectors of the electronic stress tensor, whose divergence gives the tension density, in the bonding region play important roles for characterizing types of chemical bonding such as covalency [1, 23], metallicity [24, 26, 31], and semi-metallicity [30].

In this work, we take benzenedithiol (BDT) as an example for the numerical demonstration of this balance between the tension density and the Lorentz force density in a nonequilibrium steady state, where a nonzero electronic current exists. This molecule is widely used for the study of conduction properties by first principles calculations.

This paper is organized as follows. In the next section, we review our formalism based on Rigged QED and define local physical quantities. Then we show the relation between the tension density and the Lorentz force density. In § 6.3, our computational detail is explained. Particularly, we summarize our computation method to derive several physical quantities. Then we show our computational results of the Lorentz force density and the tension density in § 6.4. We study the balance between these two densities. The last section is devoted to our conclusions.

6.2 Theory

In this work, the tension density is investigated in a viewpoint of a counter force to the Lorentz force density. The tension density operator is defined in the time-differential equation of the kinetic momentum operator [1–3],

$$\frac{\partial}{\partial t} \hat{\Pi}(x) = \hat{\tau}^\Pi(x) + \hat{\mathbf{L}}(x), \quad (50)$$

where $x = (ct, \mathbf{r})$. The first term is the tension density, and its definition is given by

$$\hat{\tau}^{\Pi k}(x) = \frac{i\hbar c}{2} \partial_l \left[\hat{\psi}(x) \gamma^l \hat{D}_k(x) \hat{\psi}(x) + h.c. \right], \quad (51)$$

where $\hat{\psi}(x)$ is the four-component Dirac field, $\hat{\bar{\psi}} = \hat{\psi}^\dagger \gamma^0$, γ^0 and γ^l are gamma matrices, $\hat{D}_k(x)$ is the covariant derivative, c is the speed of light in vacuum, $\hbar$ is the reduced Planck constant. In the nonrelativistic limit, we denote the tension density in the following form,

$$\hat{\tau}^{Sk}(x) = \frac{\hbar^2}{4m} \partial_l \left[\hat{\psi}^\dagger(x) \hat{D}_k(x) \hat{D}_l(x) \hat{\psi}(x) - \left(\hat{D}_k(x) \hat{\psi}(x) \right)^\dagger \hat{D}_l(x) \hat{\psi}(x) + h.c. \right]. \quad (52)$$

In our computations, we use this expression. The difference between two forms of the tension density is known to give the time-evolution of the spin vorticity. [24, 25, 32, 33]

The second term of eq. (50) is the ordinary Lorentz force density, which is defined as

$$\hat{\mathbf{L}}(x) = \hat{\mathbf{E}}(x) \hat{\rho}(x) + \frac{1}{c} \hat{\mathbf{j}}(x) \times \hat{\mathbf{B}}(x), \quad (53)$$

where $\hat{\mathbf{E}}(x)$ is the electric field, $\hat{\rho}(x)$ is the electronic charge density, $\hat{\mathbf{j}}(x)$ is the electronic charge current density, and $\hat{\mathbf{B}}(x)$ is the magnetic field.

In steady states, whether or not the electric current exists, the expectation value of the left-hand side of eq. (50) is zero, and hence it is seen that the Lorentz force density cancels out the tension density as

$$0 = \langle \hat{\tau}^S(x) \rangle + \langle \hat{\mathbf{L}}(x) \rangle = \boldsymbol{\tau}^S(x) + \mathbf{L}(x). \quad (54)$$

Therefore, the steady electronic current is maintained by the tension density against the constant acceleration of the Lorentz force. In this expression, $\langle, \rangle$ means the state vector, bra and ket. In

the following, we drop $\langle, \rangle$ for expectation values as the last form of eq. (54), and we can discriminate between expectation values and operators by the existence of the hat mark “” which means an operator. The definition of the tension density originates in the differentiation of the kinetic momentum and hence its origin is apparent and straightforward. Hence, we do not rely on the phenomenological assumption, such as the introduction of the relaxation time. In addition, our equation is defined in quantum field theory, and hence it is valid at any point in a material.

Previously we have used the tension density for the purpose of the study of the properties of static molecules. In this work, we want to expand the study with the tension density to nonequilibrium electrical conduction states. Electrical conduction is caused by an external electric field, which is made by a potential difference between electrodes on both sides, that is a bias voltage. The tension density and the Lorentz force density are not zero without the external electric field, since there is an internal electric field caused by the difference of the density distributions of nuclei and electrons. Accordingly, the modification of the tension density and the Lorentz force density by an external electric field should be considered.

The change of the tension density by a bias voltage is easily computed by using ket vectors with and without the bias voltage. However the computation of the modification of the Lorentz force density is not so simple, since in addition to an electronic state, an electric field is also changed due to the variation of polarization. The change of the Lorentz force density $\Delta \mathbf{L}(x)$ by the variation of an external electric field $\Delta \mathbf{D}(x)$ is given as

$$\Delta \mathbf{L}(x) = \Delta(\mathbf{E}(x)\rho(x)), \quad (55)$$

where we neglected the term, $\frac{1}{c}\hat{\mathbf{j}}(x) \times \hat{\mathbf{B}}(x)$. The variation of $\Delta \mathbf{D}(x)$ induces the variation of the polarization and therefore this is not simply given as a form proportional to $\Delta \mathbf{D}(x)$. Equation (55) is reduced to a form,

$$\Delta \mathbf{L}(x) = \Delta \mathbf{E}(x)\rho_0(x) + \mathbf{E}_0(x)\Delta \rho(x) + \Delta \mathbf{E}(x)\Delta \rho(x), \quad (56)$$

where the subscript “0” means the value without the bias voltage and $\Delta \mathbf{E}(x)$ and $\Delta \rho(x)$ are the variations of the electric field and the electronic charge density, respectively. The electric field $\mathbf{E}(x)$ is related to the external field $\mathbf{D}(x)$ as

$$\mathbf{E}(x) = \epsilon^{-1}(x)\mathbf{D}(x), \quad (57)$$

through the local dielectric constant tensor, $\epsilon(x)$. This tensor is widely treated in many literatures as a constant or diagonal matrix for bulk matter and, however, for most points in a molecule or condensed matter off-diagonal elements cannot be neglected, since directional symmetry generally does not exist at a certain point in a molecule or matter though macroscopically they have some symmetry. Hence eq. (56) is reduced to

$$\Delta \mathbf{L}(x) = \epsilon^{-1}(x)(\Delta \mathbf{D}(x)\rho_0(x) + \mathbf{D}_0(x)\Delta \rho(x) + \Delta \mathbf{D}(x)\Delta \rho(x)). \quad (58)$$

In another form, the electric field $\mathbf{E}(x)$ is given by

$$\mathbf{E}(x) = \mathbf{D}(x) - 4\pi\mathbf{P}(x), \quad (59)$$

where $\mathbf{P}(x)$ is the polarization density. The definition of $\hat{\mathbf{P}}(x)$ is as follows [2],

$$\hat{\mathbf{P}}(x) = \frac{1}{4\pi}\text{grad}\hat{A}_{0_A}(x). \quad (60)$$

The zeroth component of the four-component photon field, $\hat{A}_{0A}(x)$, is given as

$$\hat{A}_{0A}(x) = \int_A d^3\mathbf{s} \frac{\sum_a \hat{\rho}_a(\mathbf{s})}{|\mathbf{r} - \mathbf{s}|}. \quad (61)$$

where A means the system region and the sum of $\hat{\rho}_a$ takes all contribution, electrons and nuclei. A finite region is chosen for the region A , and hence the contribution from the other region M gives the external electric displacement $\mathbf{D}$ for the system. From this relation, the variation of the Lorentz force density is given as another form,

$$\Delta \mathbf{L}(x) = (\Delta \mathbf{D}(x) - 4\pi \Delta \mathbf{P}(x))(\rho_0(x) + \Delta \rho(x)) + (\mathbf{D}_0(x) - 4\pi \mathbf{P}_0(x))\Delta \rho(x). \quad (62)$$

In this work, we compare the variation of the Lorentz force derived by these two equations, since the computation of $\epsilon(x)$ is difficult as explained below. For convenience, we call the expression of the Lorentz force density based on eq. (58) $\Delta \mathbf{L}_\epsilon$, and that of eq. (62) is called $\Delta \mathbf{L}_P$.

The dielectric constant tensor $\epsilon(x)$ is considered to be computed for conduction states to use eq. (58) for conduction phenomena. This is calculated from the difference of quantum states between nonequilibrium steady states. Hence it is difficult to compute correctly even in first principles computations. Particularly the computation of off-diagonal elements are difficult. For example, no suitable code is available for a computation that electrodes are set for z -direction in a model and an extra external electric field in addition to a bias voltage is imposed on x -direction. Hence the dielectric constant density for zero bias voltage and no conduction is substituted for our computation. For this computation, $\epsilon(x)$ cannot directly be computed in our code. By using eqs. (57) and (59) and

$$\mathbf{P}(x) = \boldsymbol{\alpha}(x)\mathbf{D}(x), \quad (63)$$

the dielectric constant tensor is cast into another relation,

$$\epsilon(x) = \frac{1}{1 - 4\pi\boldsymbol{\alpha}(x)}. \quad (64)$$

In this study, $\epsilon^{-1}(x)$ in eq. (58) is computed as $1 - 4\pi\boldsymbol{\alpha}(x)$ by this equation.

6.3 Computational Detail

Our formulation described in the previous section is based on QED, and hence our quantum conduction states should be described in terms of quantum field theory. The computation code based on QED is now developed in our laboratory, which is named QEDynamics [34]. Conduction states and electromagnetic field should be consistent with the Maxwell equation, i.e. the equation of motion of the photon field. In our code, however, its computational time is too long to finish the computation and an efficient computation procedure is now invented. Hence states consistent with QED is not available yet, and we use a computational code based on the nonequilibrium Green's function method [35–37] as a substitution in this work. Methods based on the Green's function are widely used for the computation of global conductivity and current of nanosize materials and molecules [38–42]. For deriving the linear response for perturbation, we use an extension of coupled perturbed Hartree-Fock (CPHF) equations [43,44] to a non-Hermitian perturbation, which is reported in our previous works [18,19]. The choices of parameters are also summarized in the papers. Even from quantum states based on quantum mechanics by this code, it can be confirmed numerically the balance between the Lorentz force density and the tension density.

The CPHF computation is performed for the electronic structure derived by ordinary self-consistent field (SCF) computation. This SCF computation is performed by Gaussian 09 [45]. For the purpose of a demonstration, we choose BDT as an example for the confirmation of the tension density as the

counter force to the Lorentz force density. The basis set cc-pVTZ is chosen [46–50]. The structure of BDT is optimized by a Hartree-Fock computation without electrode atoms. The CPHF computation for nonequilibrium Green’s function method is carried out by our program package QEDynamics. In this computation, the sulfur atoms at the both ends of BDT are considered to be connected to electrodes which consist of a gold atomic chain. The coupling between gold and sulfur atoms and other computational detail are given in our previous works [18, 19].

In the computation of the Lorentz force density, we ignore the exchange effect, which comes from four creation-annihilation operators in the $\hat{\mathbf{P}}\hat{\rho}$ term, since the definition of $\hat{\mathbf{P}}$, eq. (60), includes also $\hat{\rho}$. This effect is not negligible and, however, requires high computational cost. Accordingly we could not include this effect, and will include it in our future work.

In the computation of the Lorentz force density based on eq. (58), we use the local dielectric constant density tensor, which is computed through eq. (64). In the correct treatment, polarizability density tensors at a certain bias voltage may be calculated with three conduction states perturbed by extra external fields $\Delta D^i(x)$. Note that since conductivity depends on a bias voltage nonlinearly, the polarizability and dielectric constant does not have simple linear dependence. This computation is not available in our code yet. Hence in this work, polarizability density tensors at a zero bias voltage without conduction are substituted for our demonstration, and we compare results of the Lorentz force density by this approximation with those based on eq. (62). In the computation of this linear response, a universal electric field $\mathbf{D}$ is used for $\mathbf{D}(x)$. First, the polarizability density tensor can be derived as

$$\Delta P^i(x) = \alpha^{ij}(x) \Delta D^j. \quad (65)$$

where $i, j = x, y, z$. The polarization $\Delta P^i(x)$ is computed by the definition (60). By using this expression, the polarization without a bias voltage can be removed appropriately. In the computation of $\mathbf{E}_0$ at $\mathbf{D}_0 = 0$ in eq. (58), $\mathbf{E}_0 = -4\pi\mathbf{P}_0$ is used. Then for the dielectric constant density tensor we calculate its eigenvalues and their eigenvectors by the relation (64) after the eigenvalues and eigenvectors of the polarizability density tensor $\alpha^{ij}(x)$ are calculated. In this computation of α , nuclear polarization effects have not been included.

The orders of eigenvalues of the polarizability and dielectric constant density tensor are taken as follows. When all eigenvalues are real, the order of the eigenvalues is the descending order of their values. On the other hand, when the eigenvalues include complex values, the real eigenvalue is set as the first one and two complex values are the second and third ones. The magnitude of the imaginary part is represented by the argument θ defined as follows,

$$\theta = \sin^{-1} \left[\frac{|\text{Im}(\lambda_i)|}{|\lambda_i|} \right], \quad (66)$$

where λ_i is the corresponding eigenvalue.

For this computation of the polarizability, stand-alone BDT is not suitable and BDT connected to gold atomic chain should be used. However this is not easy to compute by our program package. Hence we use the model that two Au atoms are added to sulfur atoms at the both ends of BDT. The LanL2DZ basis set is chosen for Au atoms [51–53]. We have compared this model with other BDT models with hydrogen termination and no termination in terms of charge distribution and density-of-state. The gold termination model gives similar values to those derived by the CPHF computation of nonequilibrium Green’s function method with a zero bias voltage by OPENMX [54, 55]. As a result, the model with two Au atoms shows good consistency with the result by using OPENMX and we adopt this model.

6.4 Results

In Fig. 1, the tension density and the Lorentz force density $\Delta \mathbf{L}_P$ induced by a bias voltage 1.00 V are shown for the $x = 0$ and $x = 1.09$ bohr planes. Here $x = 1.09$ bohr is determined by a criterion that

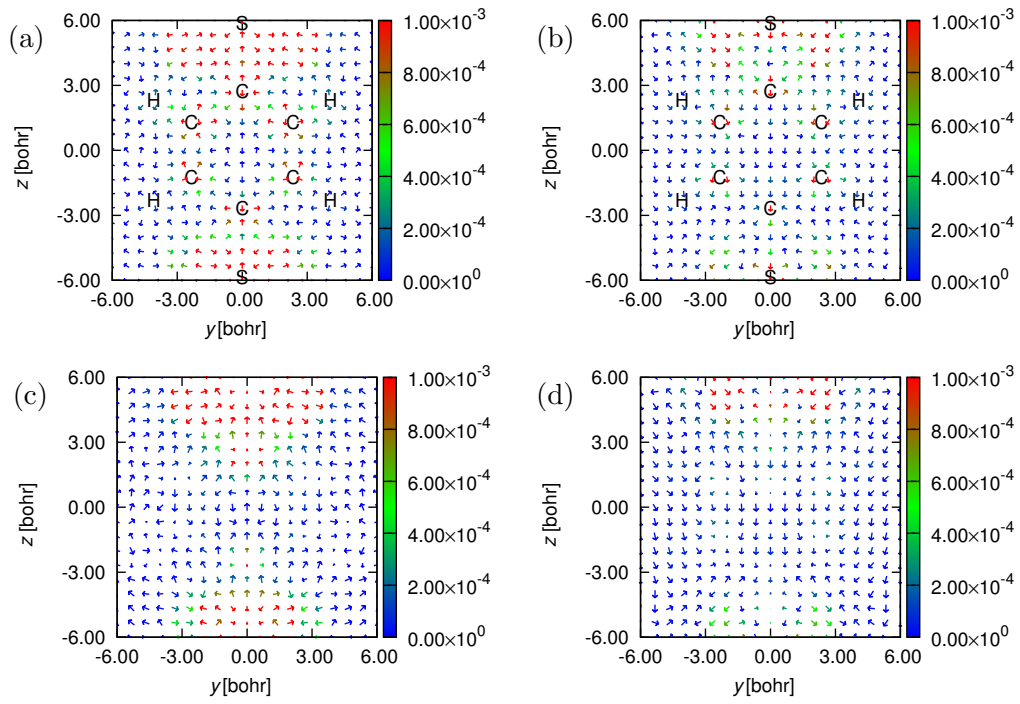


Fig. 1: The tension density induced by a bias voltage 1.00 V on $x = 0$ bohr plane (a) and $x = 1.09$ bohr plane (c). The Lorentz force density $\Delta \mathbf{L}_P$ induced by the bias voltage on $x = 0$ bohr plane (b) and $x = 1.09$ bohr plane (d). The units are atomic units.

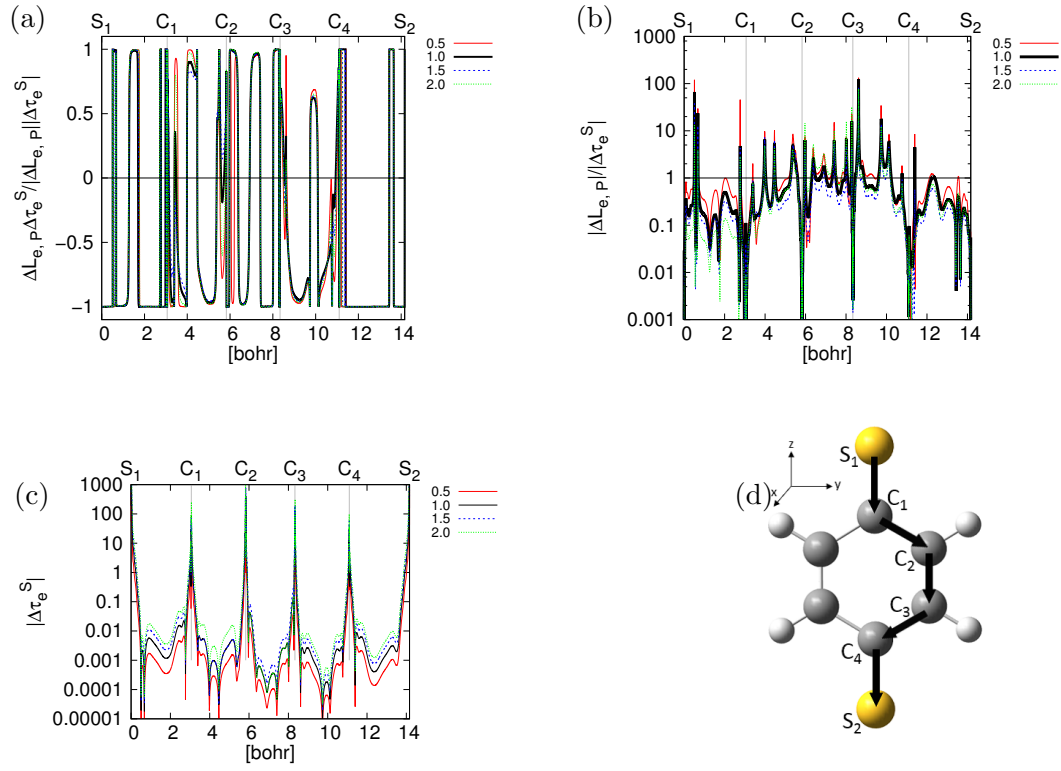


Fig. 2: (a) The angle between the tension density and the Lorentz force density is shown as the cosine form. (b) The ratio of the norm of that of the Lorentz force density to the tension density. In these two panels, the horizontal axis is the route shown in panel (d). (c) The norm of the tension density. (d) The route used in panels (a), (b) and (c).

the electron density of the highest occupied molecular orbital is the largest for $z = 0$ bohr which is the middle of two carbon atoms. The color and direction of arrows mean the magnitude and direction of the tension density and the Lorentz force density. In this figure, most vectors of the tension density have opposite direction to those of the Lorentz force density particularly around neighborhoods of nuclei where the accuracy of computations is better compared to other region. The distribution pattern of them are roughly similar to each other and the values of them are also close to each other. In Figs. 2(a) and (b), the balance between the tension density and the Lorentz force density is shown along the line (panel (d)) between two sulfur nuclei through four carbon nuclei on the benzene ring. This line is chosen as a reference to compare the two densities in a quantitative form, since this line represents some of chemical properties of this molecule. In panel (a), the angle between the tension density and the Lorentz force density is shown as a cosine function. The directions of these two densities should be opposite and the value of the cosine should be -1 ideally in the steady state. From this figure, values are -1 or negatively large in most region. However, positive large value of cosine is seen in some points. This is caused by the shift of a boundary where the direction of a vector is reversed, for example this occurs around a nucleus. In two computations of the tension density and the Lorentz force density these boundaries are often deviated, and hence a boundary shift results in the same direction vectors. This boundary can be seen as points at minima in panel (c). At a minimum with a very small tension density value, the tension density is known to often reverse the direction. [26, 28–30] Almost all positive cosine values are seen to be related to these points or nuclear positions, and hence our explanation is reasonable. As a result, our computations are considered to show the opposite feature between the directions of the tension density and the Lorentz force density. In addition, the accuracy is worse for the point at a nucleus, since a combination of Gaussian functions in place of a Slater type function are used in our computations. Hence the balance may be worse around nuclei. In panel (b) the ratio of the norms of the tension density and the Lorentz force density is shown along the line. For the values of these densities, very large or small values are seen for some points and the cancellation is not clearer compared to the directions. Nevertheless, in most region between carbon atoms the discrepancy is not so large. The values at nuclei are very small, almost zero, and this is attributed to the accuracy at a nucleus as explained above. Some peaks in this figure correspond to peaks in panel (c), and hence it is reasonably seen that the ratio is often deviated from one at points that the tension density is very small than about 10^{-5} a.u. For $x = 1.09$ bohr, the balance between two densities is worse compared to the $x = 0$ bohr plane as seen from Figs. 1(b) and (d), since the accuracy of our computations is worse compared to the $x = 0$ bohr plane. Hence we can confirm the balance between the tension density and the Lorentz force density. However, the cancellation between them is not exact though the steady state is assumed. This is because we did not use the exact quantum state of quantum field theory. In particular, we ignored the exchange effect in the Lorentz force density. Moreover some numerical errors exist as mentioned above.

In Fig. 3, the current density distribution induced by a bias voltage 1.00 V is shown for the $x = 0$ and $x = 1.09$ bohr planes. As reported in our previous work [19], the current density is large on $x = 1.09$ bohr plane due to the contribution from π bonding. From the comparison between Figs. 1 and 3, the distribution of the tension density is independent of that of the current density. For example, in the Drude model, a counter term to the Lorentz force is assumed to be friction and the counter term is proportional to the velocity of the electron. When the Drude model is naively extended to microscopic viewpoint, the distribution of the counter force is proportional to the current density. Our result show that this naive extension is not allowed, even if the assumption of the friction term in the Drude model is successful for a macroscopic viewpoint. From eq. (58), the change of the Lorentz force density by a small bias voltage is almost proportional to $\epsilon^{-1}(x)\Delta\mathbf{D}(x)\rho_0(x)$. In our case, since $\Delta\mathbf{D}(x)$ is assumed to be universal $\Delta\mathbf{D}$, it is almost proportional to $\epsilon^{-1}(x)\Delta\mathbf{D}\rho_0(x)$, and the distribution of the counter force is governed by the dielectric constant tensor and the charge density.

The results in Fig. 1 are the changes of the tension density and the Lorentz force density induced by a bias voltage. Even without a bias voltage, the Lorentz force density has a nonzero value locally

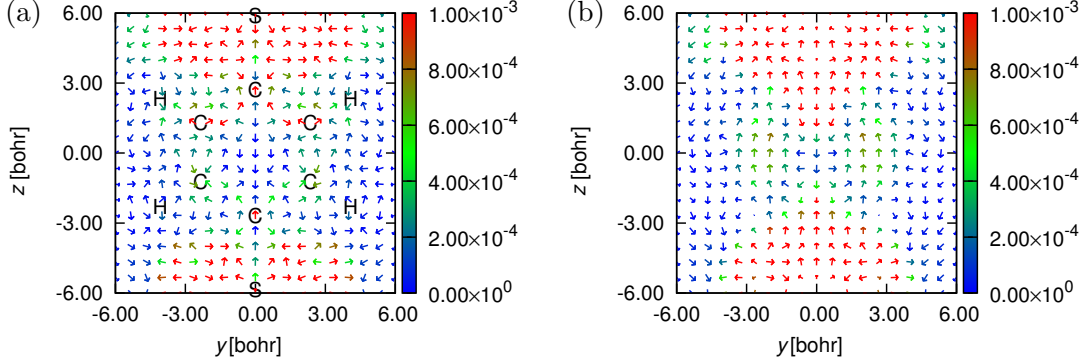


Fig. 3: The current density induced by a bias voltage 1.00 V on $x = 0$ bohr plane (a) and $x = 1.09$ bohr plane (b). The units are atomic units.

in BDT, and hence the tension density is also nonzero. The tension density without any bias voltage has been studied in our previous works [6, 26–30, 56–59]. Figure 4 shows the tension density and the Lorentz force density without a bias voltage. The balance between them can be seen in this figure too. The Lorentz force density is larger around nuclei, since both the charge density and the electric field are large. Hence the tension density is also large around nuclei. The Lorentz force density has the direction toward a nucleus as expected from the charge of the nucleus, while the direction of the tension density is opposite. The values of the norm of these density are much larger than those in Fig. 1. The results in Fig. 1 are the changes of quantities induced by a bias voltage as perturbation, while those in Fig. 4 are unperturbed ones. Hence this difference of the order is attributed to the magnitude of the perturbation parameter, that is, the difference between the internal electric field and the electric field induced by a bias voltage. The electric field by the discrepancy between the positive and negative charge density in a molecule is much larger than the electric field by a bias voltage. The former is about 1 a.u. (5.1×10^{11} V/m), while the other is about 0.002 a.u. (9.4×10^8 V/m). The difference of the magnitude between Figs. 1 and 4 is attributed to this difference. The exact cancellation between the tension density and the Lorentz force density is not seen as those change induced by a bias voltage and this reason is also the same as Fig. 1.

In Fig. 1, we have shown the result based on eq. (62). Figure 5 shows the Lorentz force density $\Delta \mathbf{L}_\epsilon$ induced by a bias voltage 1.00 V. By comparing with Fig. 1, we can see that the distribution pattern is highly similar and the value of the Lorentz force density shows good agreement. This feature is seen in both planes on $x = 0$ and 1.09 bohr. Even though we have used simple approximations for the computations of the dielectric constant density tensor, the estimate of the Lorentz force density is acceptable. As only an exception, the directions of the Lorentz force density is opposite in the inside of the benzene ring, where our computation is less accurate than that around nuclei. This difference is dominantly attributed to the difference of the estimate of $\Delta \mathbf{E}(x)$ between $\epsilon^{-1} \Delta \mathbf{D}$ and $\Delta \mathbf{D} - 4\pi \Delta \mathbf{P}$. In our computations of the dielectric constant tensor density, some assumptions are adopted, and hence we check the dielectric constant tensor density itself.

In Fig. 6, the dielectric constant tensor density ϵ is shown on $x = 0$ bohr plane. In regions enclosed by lines, the eigenvalue is complex. In these regions, the dielectric response to an external electric field has rotational behavior [7–9]. These regions are seen around carbon and sulfur atoms widely. These properties cannot be seen in the ordinary averaged analysis. This can only be described correctly in the local and tensor analysis. In panel (c), in the inside of the benzene ring, the dielectric constant tensor density is negative and the direction of eigenvectors is z -direction. This negative response appears when the polarizability density is larger than $1/(4\pi)$ as seen from eq. (64). The first eigenvalue of the polarizability tensor density α is shown in Fig. 6(d). In the inside of the benzene ring, the value of

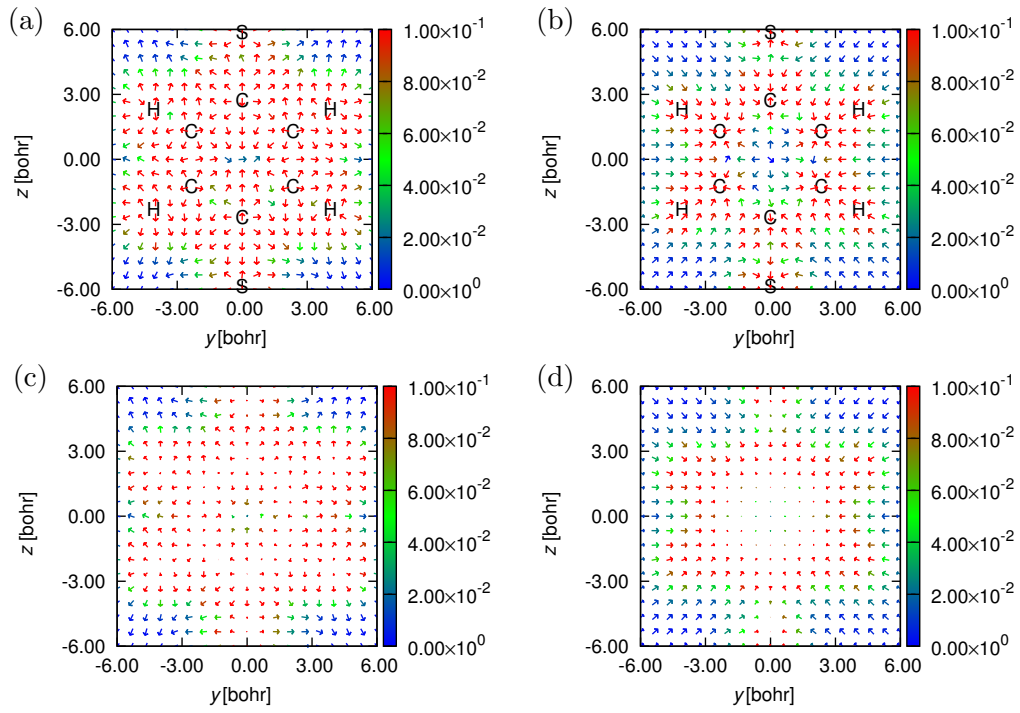


Fig. 4: The tension density without the bias voltage on $x = 0$ bohr plane (a) and $x = 1.09$ bohr plane (c). The Lorentz force density $\Delta \mathbf{L}_P$ without the bias voltage on $x = 0$ bohr plane (b) and $x = 1.09$ bohr plane (d). The units are atomic units.

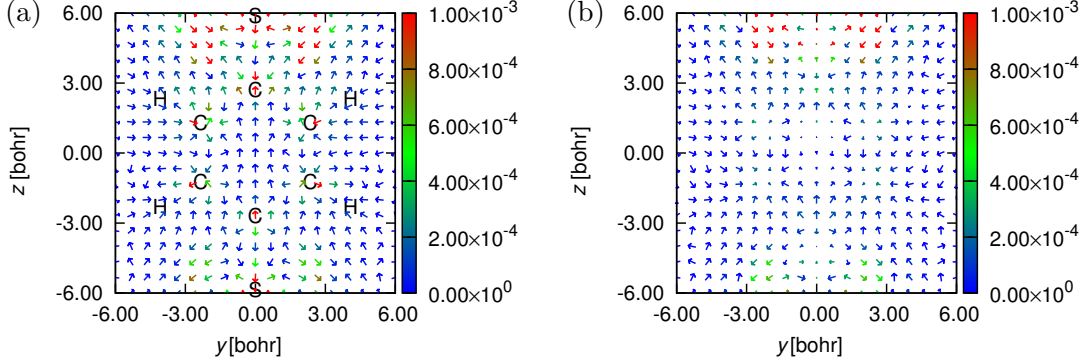


Fig. 5: The Lorentz force density $\Delta\mathbf{L}_\epsilon$ induced by a bias voltage 1.00 V on $x = 0$ bohr plane (a) and $x = 1.09$ bohr plane (b). The units are atomic units.

the polarizability tensor density is seen to be large. This result may indicate that in our approximation that the dielectric constant density is computed for a zero bias voltage, the polarizability tensor density and the dielectric constant tensor density are not computed accurately. In our next work, we will try some improvement and continue to judge our approximations.

Finally, the dependence on a bias voltage is discussed. In Fig. 2(a), the angle between the tension density and the Lorentz force density is shown for four bias voltages. The shape of the lines are similar to each other. As explained above, points with positive values originates in a boundary shift due to the unavoidable shortage of precision. This figure confirms the balance between two densities independent of a bias voltage. In Fig. 2(b), the ratio of the norms of the tension density and the Lorentz force density is shown for the four bias voltages. The ratio is more dependent on a bias voltage, and nevertheless in most regions the value of the ratio is around one.

6.5 Conclusion

It is confirmed numerically that the tension density defined in quantum field theory is the counter force to the Lorentz force density. Benzenedithiol has been taken as an example for the numerical demonstration of the balance between these densities. For a conduction state, that is a nonequilibrium steady state, we have used simply a nonequilibrium Green's function method. This method is not appropriate for our purpose. For example, a polarization effect by a bias voltage is not included correctly. Nevertheless the balance between the tension density and the Lorentz force density has been confirmed. The tension density is free from the relaxation time ansatz and defined as a local quantity. The tension density may give a novel viewpoint to the understanding of the physics of electrical conduction.

In the future work, we must include the exchange effect in the computation of the Lorentz force density. In this work, while a nonequilibrium Green's function method is used, we should use a better computational method to represent a conduction state.

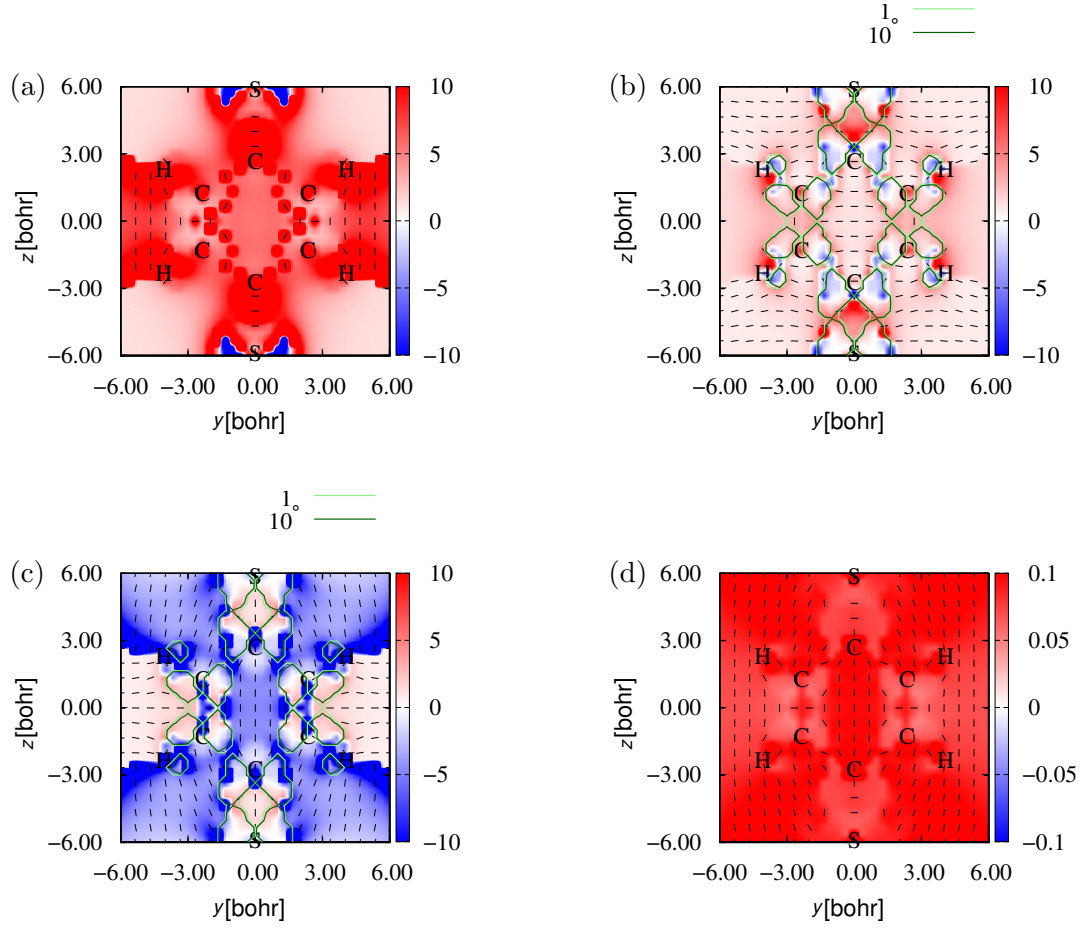


Fig. 6: The dielectric constant tensor density ϵ on $x = 0$ bohr plane. Panels (a), (b), and (c) are the first, second, and third eigenvalues and eigenvectors, respectively. Panel (d) shows the first eigenvalues and eigenvectors of the polarizability tensor density α on $x = 0$ bohr plane. The color and short line mean the eigenvalue and the direction of the eigenvector, respectively. In the region enclosed by lines, the eigenvalue is complex. The units are atomic units.

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General Conclusion

In this thesis, I have investigated atomic and molecular systems by local physical quantities defined in Rigged QED. The local physical quantities I use in this thesis is shown below: the electronic kinetic energy density, electronic stress tensor density and related quantities such as eigenvalues and eigenvector of stress tensor density and tension density. By using these quantities, I can obtain many important information which is related to electronic structure.

In Chapter 1, electronic structure of atoms in the first, second and third periods are analyzed by the electronic kinetic energy density and electronic stress tensor density. I use the concept of the electronic interface S , where the electronic kinetic energy density is zero, to investigate the shape of atom. From this analysis, I find the shape of outermost $S(S_{outer})$ coincides with the symmetry expected from the configurations of electron of each atom. I also show that, some atoms can be separated into core and valence region by S . I denote the surface of core shell as S_{inner} . Through the investigation of S_{outer} and S_{inner} , it is shown that the size of them have clear periodicity with nuclear charge. I also find the tendency of the tension density. The tension density of all atoms I have examined, has the vector field points from the nucleus to outside of the atom. This result implies the tension density of each atomic pair makes separatrix, the boundary of the tension density.

Chapter 2 is devoted for the analysis of small lithium clusters and hydrocarbon molecules using the electronic stress tensor density. From the viewpoint of the eigenvalues of the electronic stress tensor density at the “Lagrange point” (where tension density is zero between two atoms), I show the chemical bond of Li cluster has very much different pattern from that of hydrocarbon molecules. While three eigenvalues of hydrocarbons are not degenerated, the eigenvalues of lithium clusters are all negative and have almost same value. This pattern of degenerated eigenvalues indicates that bond has not directional. It is able to consider that, this pattern reflects the nature of bonding of Li clusters as “metallic” bond. To evaluate this degeneration of eigenvalues quantitatively, I have proposed the differential eigenvalues. Through the demonstration of the results of Li clusters and hydrocarbon molecules, these differential eigenvalues are shown as useful tool to evaluate the degeneration of eigenvalues.

Chapter 3, 4 and 5, I discuss how chemical bonds made by Ge, Sb, and Te atoms and Ga nano-clusters (Ga_{12}X) are expressed with the differential eigenvalues demonstrated in Chapter 2. As a result, chemical bonds made by Ge, Sb and Te atom exhibit intermediate degeneration pattern between alkali metal clusters and hydrocarbon molecules, when I use the differential eigenvalues at the Lagrange point of each chemical bond. This result consistent with the classification of Ge, Sb, and Te atom as “metalloids”. In Chapter 3, I show the positive correlation between force constant and our bond order b_ε , which is defined from the value of the energy density at the Lagrange point. The energy density is calculated from the eigenvalues of the electronic stress tensor density. I also show the Lagrange surface, where tension density makes separatrix between two atoms, can separate molecule into atomic own region.

In Chapter 4, I propose the alternative bond order $b_{\varepsilon(S)}$. This bond order is defined by the energy density in the Lagrange surface. I find that both bond order has strong correlation between force constant, but has weak correlation between bond dissociation energy.

I show how Ga nano-clusters are expressed with the electronic stress tensor density in Chapter 5. The degeneration pattern of eigenvalues of these clusters have also intermediate pattern between alkali metals and hydrocarbon molecules.

In Chapter 6, the tension density in the conduction state, that is a nonequilibrium steady state, is discussed. As it is already numerically confirmed that the tension density is the counter force of the Lorentz force density, the cancellation between the tension density and the Lorentz force density is confirmed. Because the tension density is free from the relaxation time ansatz and defined as a local quantity, it is useful tool to understand the physics of electrical conduction.

As a result of these works, the local physical quantities based on Rigged QED are shown as powerful tools for understanding electronic structures of atomic and molecular systems.

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List of Publications

Chapter 1

Hiroo Nozaki, Kazuhide Ichikawa, and Akitomo Tachibana,

“Theoretical study of atoms by the electronic kinetic energy density and stress tensor density”
Int. J. Quant. Chem. *in press*.

Chapter 2

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Chapter 3

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Chapter 4

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Chapter 5

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“Bonding in Doped Gallium Nanoclusters: Insights from Regional DFT” Comput. Materials
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Chapter 6

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- *Atomic shell structure study by kinetic energy density and stress tensor density.*
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